CHEMICAL PROCESS SIMULATION OF P-XYLENE OXIDATION IN A SPARGER REACTOR

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CHEMICAL PROCESS SIMULATION OF P-XYLENE

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PREFACE

Sparger reactors have a relatively short history in industrial operation limited mainly to the last decade, Unfortunately there is still much confusion and contradiction in the literature. There are countless recommended correlations, but little in the way of a unifying theory. Each researcher has worked on any one particular aspect of this reactor on small scale models. All of these findings have to be integrated to simulate a model for the reactor. This approach was the basis of my Master's thesis at Oklahoma State University.

My studies in the United States have given me an indepth knowledge of the American culture apart from strengthening my educational background. I must admit that I was extremely fortunate to have had Dr. Arland H. Johannes as my adviser. He was a sincere and patient instructor, whose commitment to education places student's cause above himself. I never hesitated in talking to him about my personal problems, and my respect for him goes deeper than that for a mentor and guide.

I thank Dr. Gary L. Foutch and Dr. Whiteley for having served on my committee and for their endearing presence. Special thanks to Dr. Robert L. Robinson for

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Studying abroad was not too often felt by me chiefly due to the enjoyable presence of my dear friends. If I were to thank everyone of them I would run out of both space and time. I must admit that Stillwater and OSU are truly unique in certain aspects nationwide and I wish to acknowledge all those people who made my stay in Stillwater memorable.

My parents Mr. W. Somasundaram and Mrs. W. S. Kannibai deserve adoration for all their love and sacrifice, and so do my friends and relatives back home. Special thanks to my brother Anand and sister Aruna with whom I shared more than a common roof. I thank all my friends and relatives without whose cooperation this study wouldn't be possible.

Looking back many years from now, I am sure my stay in Stillwater will evoke pleasant memories.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

NOMENCLATURE

C_A	Concentration of A, Kgmole/m^3
C_{A0}	Initial concentration of A, Kgmole/m^3
C_{Af}	Final concentration of A, Kgmole/m^3
D_{AB}	Diffusion coefficient, cm^2/s
D_{bed}	Diameter of bed, meters
D_b	Diameter of bubble, meters
d_0	Diameter of orifice, meters
F_{A0}	Molar flow rate of A, Kgmoles/s
g	Acceleration due to gravity, m/s^2
K, K_r	Rate constant
K_{bc}	Mass transfer coefficient between bubble and cloud, s^{-1}
K_{ce}	Mass transfer coefficient between cloud and emulsion, s^{-1}
K_f	Reaction rate group for fluidized bed
L_f	Length of reactor, meters
m_b	Fraction of solids in bubble
N_{A0}	Initial moles of p-xylene, Kgmoles
(P/V)	Work done, W/m^3
-rA	Rate of reaction, Kgmole/m^3s
T	Temperature, K
U	Overall heat transfer coefficient, Cal/hr cm^2°C
U_0	Superficial gas velocity, m/s

U_{br}	Bubble rise velocity, m/s
U_{mf}	Minimum fluidizing velocity, m/s
V	Volume of reactor, m^3
v	Volumetric flow rate, m^3/s
V_b	Volume bubble, m^3
V_{bs}	Single bubble velocity, m/s
V_g	Velocity of gas, m/s
V_l^c	Velocity of liquid, m/s
V_s	Superficial gas velocity, m/s
V_w	Volume of wake, m^3
X_A	Conversion of A
X_{Af}	Final conversion of A
τ	Residence time, s
τ_b	Ratio of solids in bubble to volume of bubbles
τ_c	Ratio of solids in cloud to volume of bubbles
τ_e	Ratio of solids in emulsion to volume of bubbles
ϵ	Void fraction
ϵ_{mf}	Void fraction at minimum fluidizing conditions
δ	Fraction of beds consisting of bubbles
σ	Surface tension, $Dynes/cm^2$
P	Density of liquid, Kg/m^3
ϕ_l	Liquid mixing, m^3/s

CHAPTER I

INTRODUCTION

In the last decade, a large amount of research was done on the use of spargers as a surrogate for mechanical agitation. The present scope of such replacement is limited to low viscosity liquid systems. Sparger type reactors find application in many chemical industries and biotechnology processes such as the production of baker's yeast, wastewater management, single cell protein (SPC) production, and citric acid production [1].

Spargers are used in a variety of processes as a contacting apparatus to obtain mass transfer with or without chemical reaction. Spargers are bubble columns which negate the need for mechanical agitation, thereby eliminating the disadvantage of moving parts. Use of spargers results in better circulation, i.e. more efficient mixing which is needed for efficient chemical reactors.

The basic mechanisms taking place in a bubble column are the formation of bubbles, bubble rise and the resulting circulation. These mechanisms influence the flow pattern which influences mixing, heat and mass transfer.

Of late, spargers have found application in the manufacture of dimethyl-terephthalate [2]. Manufacture of dimethyl-terephthalate involves the oxidation of p-xylene over modified cobalt catalyst. Air, which is widely used as the oxidizer, is bubbled through a column of liquid p-xylene.

Dimethyl-terephthalate is extensively being used as a raw material for polymers (e.g. nylon). The reaction process is as follows: a) p-xylene is oxidized to monomethyl-terephthalate at high circulation rates in an induced flow reactor loop, b) the reaction is carried out under isothermal conditions made possible by the use of heat exchangers, with maximum temperature variation within the reactor limited to about 3° - 5°F. The steps involved in the process are:

a) introduction of the liquid reactants,

b) bubbling air up through the reactor,

c) venting excess gas, and

d) cooling the reaction medium to remove the heat of reaction (exothermic).

Some variables that control the rate of oxidation of p-xylene are the cobalt concentration, temperature, pressure, mass transfer coefficients, the reactor dynamics and mixing patterns.

Despite serious drawbacks, the compelling advantages of the sparger system have been responsible for the successful use in many industrial operations.

Advantages and Disadvantages of Bubble Columns for Industrial Operations

Use of spargers in industrial applications have both desirable and undesirable characteristics. These are the factors to be considered for such a replacement.

Advantages of sparger type reactors include:

1. rapid mixing of liquid which results in isothermal conditions throughout the reactor when heat exchanger tubes are used inside the reactor,
2. mass transfer rates between gas and liquid phases are high compared to mechanical agitation, and
3. the rate of heat transfer between gas and liquid phases is high, hence the area required for heat transfer is relatively small.

Disadvantages of sparger type reactors include:

1. difficulty in describing the flow of gas through the reactor, and deviation from ideal plug flow conditions. This effect becomes predominant at high production rates.
2. rapid mixing which can lead to non-uniform residence time of the catalyst.
3. the catalyst concentration can vary, depending on the size of the reactor, due to the fluidizing conditions.

Due to the complex characteristics of this reactor, modeling of such reactors pose a great problem. Some portions of the reactor behave as a plugflow reactor while the remaining portions can be treated as a well mixed reactor.

This study investigates the mechanisms of bubble column related to three phase sparged reactors, studies the effect of the circulation patterns on the reaction kinetics and predicts industrial operating conditions.

CHAPTER II

LITERATURE REVIEW

A detailed study of the literature relevant to the manufacture of DMT in sparged reactors involved the following:

1. description of bubble columns,
2. reaction kinetics for oxidation of p-xylene,
3. process description, and
4. purification.

Bubble Column Description

The need to do away with moving parts in the reactor leads to wide usage of sparger reactors in chemical and biotechnological applications. Spargers are very energy efficient [3] and are suitable where precise temperature control is desired [4].

One of the basic phenomenon in a bubble column is the formation of bubbles at the sparger. The smaller the bubbles, the larger the area available for mass transfer between the gas and the liquid phases. Bubbles formed at the sparger increases in size as they move upward in the reactor.

The bubbles formed at the sparger rise in the form of a cloud. The behavior of the bubble cloud is determined solely by the superficial gas velocity. At low gas velocities, a fairly homogeneous distribution of rising bubbles occurs in the bubble column. This is sometimes called the "homogeneous flow regime" [3]. The fractional gas holdup, also defined as the void fraction, is defined by

$$\epsilon = \frac{V_s}{V_{bs}} \qquad (2.1)$$

where

V_s - gas superficial velocity, m/s

V_{bs} - single bubble rise velocity, m/s

Liquid mixing in a bubble column is attributed mainly to the bubbles themselves. When the bubbles rise, a certain amount of the liquid is carried along with them in the wake and some pushed upward by the rising bubble. The velocity difference around the bubble also causes liquid mixing.

The effect of liquid properties on the gas holdup is large and is dependant on the type of sparger. The liquid properties that affect the holdup are the surface tension and viscosity.

Reaction Kinetics for Oxidation of P-xylene

The rate expression is not widely available for the oxidation of p-xylene. The disappearance of oxygen

without an induction period by p-xylene at 140°C is expressed as follows [5]

$$\frac{-d[O_2]}{dt} = K \frac{[Co\ III]^{0.19}\ [PX]^2}{[PTA]^{0.21}} \qquad (2.2)$$

Where

K = rate constant, 6.5 X 10^{-5} Kgmole Sec^{-1}

[Co III] = cobalt catalyst concentration

[PX] = p-xylene concentration

[PTA] = terephthalic acid concentration

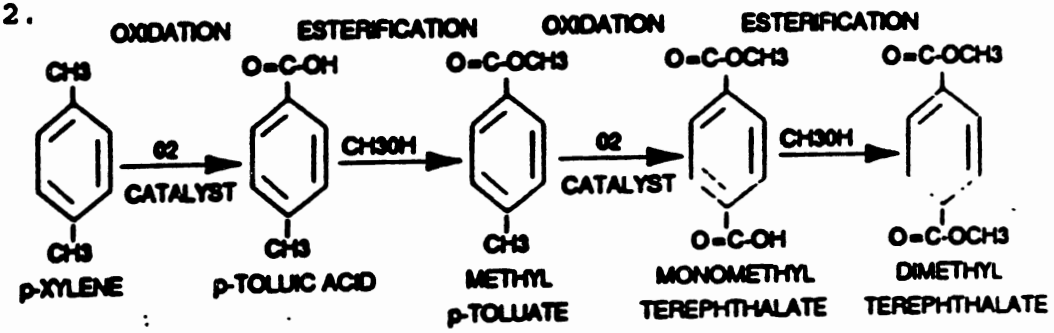
$[O_2]$ = oxygen concentration

There are several reactions possible along with the two major reactions listed below. At low temperatures, between 140 and 170°C, the manufacture of DMT follows the path of the second reaction.

1. Conversion of p-xylene to p-toluic acid and water

C_8H_{10} (p-xylene) + 1.5 O_2 (Air) ⟶ $C_8H_8O_2$ (p-TA) + H_2O

2.



Process Description

The oxidation of p-xylene in the presence of cobalt salts proceeds at temperatures above 110°C and sufficient

oxygen pressures. Usually no induction period is required, and the oxygen absorption is self catalyzed like autocatalytic reactions. The effect of initial concentration of the cobalt catalyst on the maximum absorption rate of oxygen is significant, and shows the sensitivity of the reaction to the catalyst concentration.

The manufacture of dimethyl-terephthalate is carried out by the oxidation of p-xylene at very high circulation rates in an induced flow reactor loop without mechanical agitation or pumping [6], under isothermal conditions. Maximum variation within the reactor can be limited to 3° - 5°F. The conversion of p-xylene to momomethyl-terephthalate is carried out in a reactor loop in the following manner

1. introduction of liquid p-xylene into the loop through one or more liquid inlets,
2. introduction of oxygen containing gas into the reactor column to gasify and cause circulation of the reaction medium through the loop,
3. introduction of catalyst into the reactor loop along with solid residue,
4. venting of excess gas from the top of the reactor, and
5. cooling of the reaction medium to remove the heat of reaction (exothermic).

Figures 1 and 2 present typical industrial sparger reactors. Figure 1 shows a reactor with two legs for induced circulation. Figure 2 show a single reactor with the bubble column. These reactors operate with high liquid circulation rates. The driving force for circulation is the difference in specific gravity or weight of the liquid reaction medium contained in the reactor. Unreacted oxygen and inerts are vented off the top of the loop. The excellent mixing associated with the turbulent flow results in high yields. Introduction of a substantial amount of gas ensures that the flow is in the turbulent region which is required for proper mixing and heat transfer.

Relative to improving monomethyl-terephthalate yield, it is preferred to operate at a p-xylene conversion of 20 and 50 percent. This is to reduce the amount of byproduct formation [7]. The consumption of oxygen during the oxidation process reduces the amount of oxygen reaching the top of the reactor loop. The taller the gasified section, the greater the circulation. The presence of inerts greatly increases the amount of circulation. When air is used, introduction of about 3.0 moles of oxygen, per mole of p-xylene to be oxidized results in more than adequate circulation. The typical reaction conditions are from 140°C to about 170°C and 4 to 8 atmospheres [6], these conditions have been

The labelling of the parts is as follows and are common for both figures

2. Reactor with induced circulation loop
3. Liquid reaction medium
4. Reactor column
6. Heat exchanger column
8. Gas inlet
10. and 11. Reactant inlet means
12. and 13. Connecting conduits
14. Venting section
15. Heat exchanger tubes
18. Gas-liquid interphase
19. Liquid-gas separation section
20. Oxidate outlet
21. Catalyst inlet
30. Water inlet
32. Steam outlet

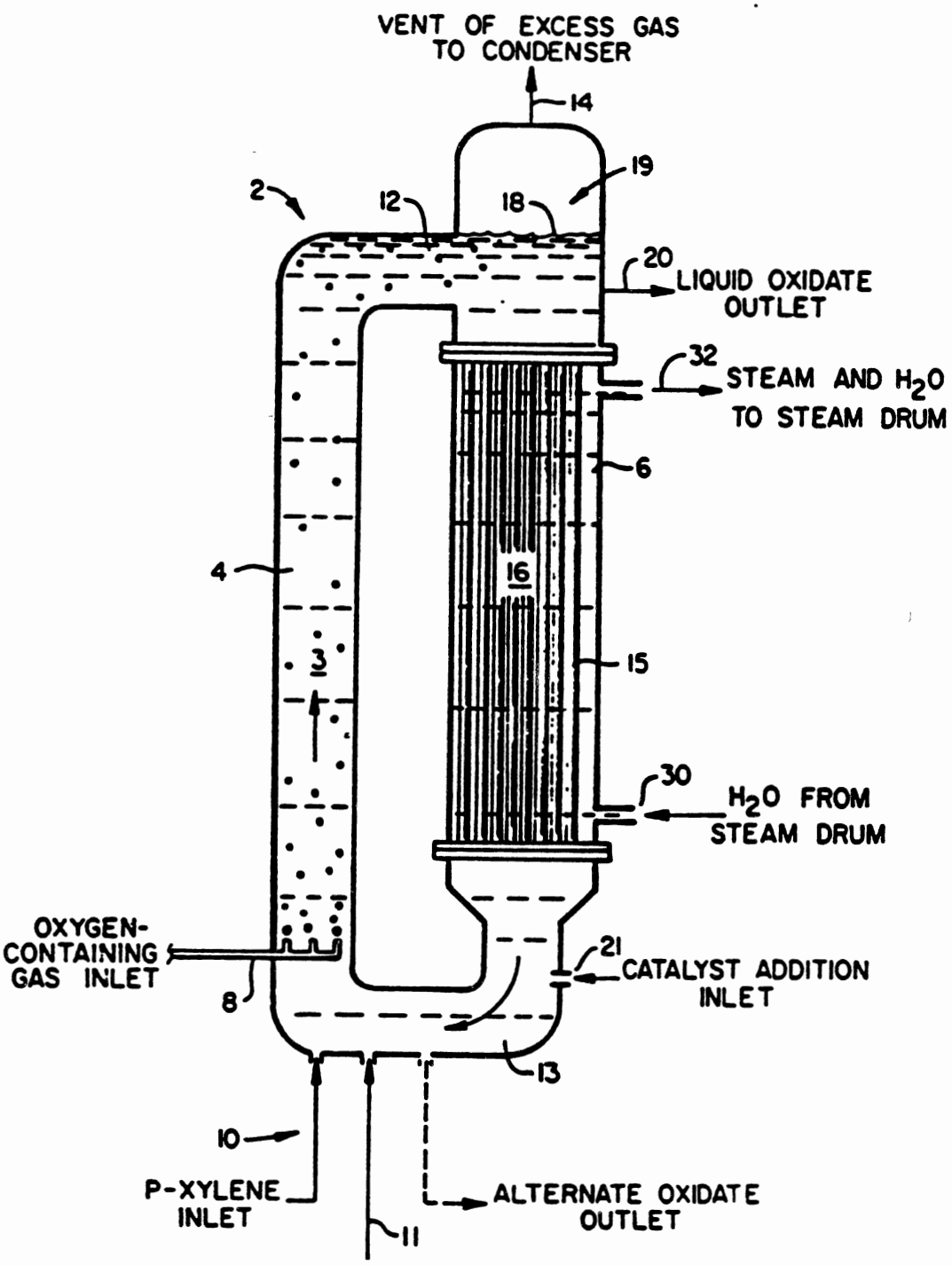


Figure 1. Reactor with separate bubble and heat exchanger loop; adapted from Klingman [2]

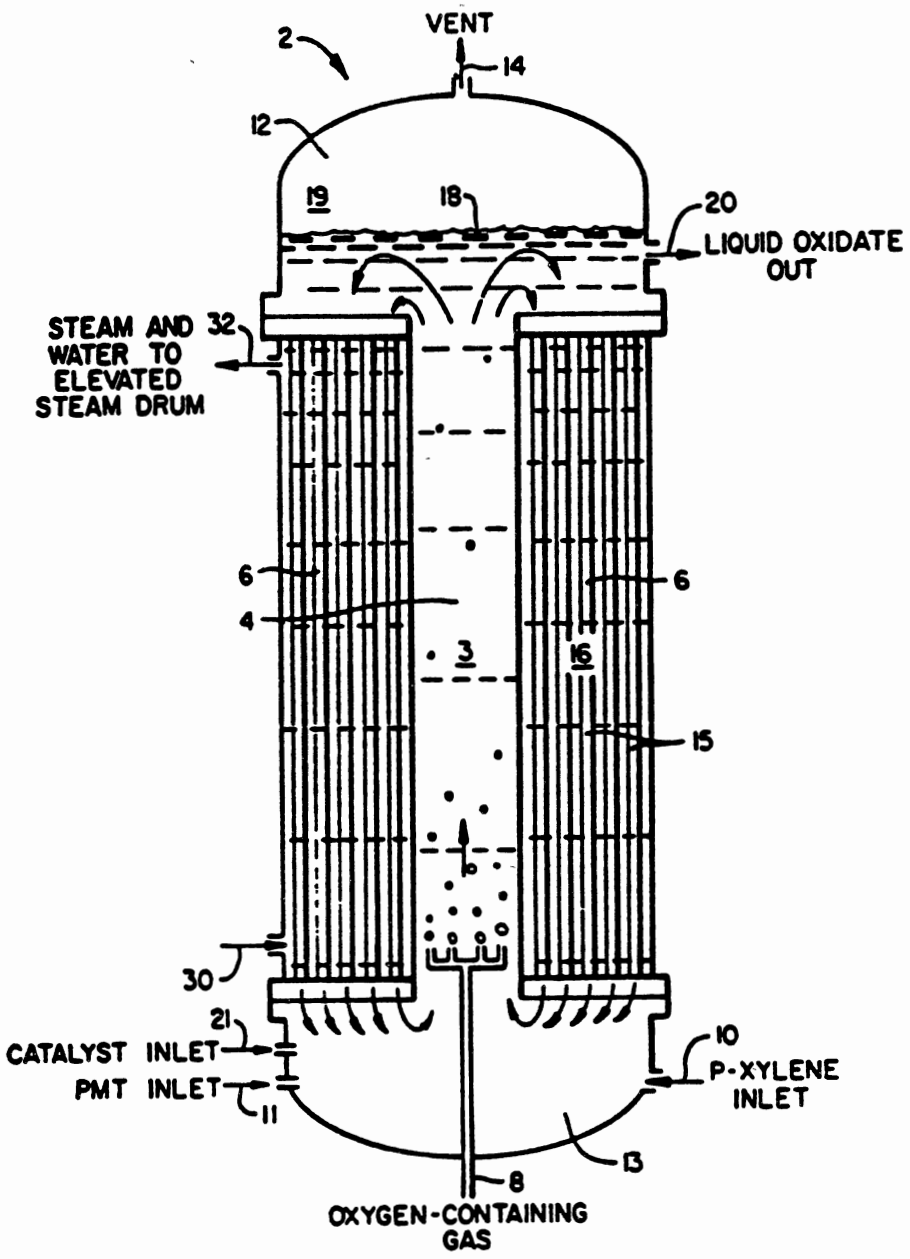


Figure 2. Reactor with induced circulation loop; adapted from Klingman [2].

optimized to reduce oxidation losses of p-xylene to carbon dioxide and water.

This reactor mechanism has an inherently low pressure drop and the wall effects on the flow of liquids through the reactor are minimal because of the large column diameter.

Purification

The reaction mixture, which is either in the crystalline or emulsion form is mixed with an appropriate solvent to dissolve all compounds except monomethyl-terephthalate. Solvent extraction is then carried out to purify the monomethyl-terephthalate (MMT).

An alternate procedure is to cool and crystallize the monomethyl-terephthalate. The molten and crystalline portions are then separated from one another. The crystallized portion is then washed with an appropriate solvent, to remove the impurities.

The MMT will still have traces of colored contaminants. These can be removed by an adsorption process [7]. The MMT is dissolved in a solvent at elevated temperatures. Suitable solvents for this process are methanol and acetone. The resulting solution of MMT is contacted with activated carbon and the colored contaminants and are removed by adsorption.

CHAPTER III

DESIGN PRINCIPLES FOR SPARGER REACTOR

The sparger reactor deviates from ideal plug flow conditions because a portion of the reactor behaves as a constantly stirred tank reactor. Hence, this reactor cannot be modelled with the performance equation for any one individual case.

Ideal Plug Flow Reactor

In a plug flow reactor, the composition of the fluid varies from point to point along the reactor length. A material balance for the reactor yields the performance equation for the plug flow reactor as follows

$$\frac{V}{F_{A0}} = \frac{\tau}{C_{A0}} = \int_0^{X_{Af}} \frac{dX_A}{-r_A} = -\frac{1}{C_{A0}} \int_{C_{A0}}^{C_{Af}} \frac{dC_A}{-r_A} \qquad (3.1)$$

$$\tau = \frac{V}{v_0} = C_{A0} \int_0^{X_{Af}} \frac{dX_A}{-r_A} = -\int_{C_{A0}}^{C_{Af}} \frac{dC_A}{-r_A} \qquad (3.2)$$

Where

τ = residence time, s

V = volume of reactor, m^3

v = volumetric flow rate, m^3/s

C_{A0} = initial concentration of A, Kgmole/m^3

F_{A0} = molar flow rate of A, Kgmole/s

X_A = conversion of A

C_{Af}, X_{Af} = final concentration and conversion of A respectively.

As discussed earlier, the rate expression for the reaction is not available. Hronec et al. [5] concluded that the rate decreases with temperature for the oxidation of p-xylene. Since the oxidation of p-xylene to MMT follows a similar mechanism as that for the oxidation of p-xylene to p-toluic acid [5], equation 2.2 was modified to

$$-\frac{d[O_2]}{dt} = 2.5 \times 10^{-5}\, e^{(413/T)}\, \frac{[PX]^2\, [Co^{III}]^{0.21}}{[MMT]} \qquad (3.3)$$

Where

[px] = p-xylene concentration, Kgmole/m^3

[Co^{III}] = cobalt catalyst concentration, Kgmole/m^3

[MMT] = monomethyl-terephthalate concentration, Kgmole/m^3

[O_2] = oxygen concentration, Kgmole/m^3

The rate expression can be represented by

$$-r_A = K\, \frac{C_{A0}^2\, (1 - X_A)^2\, (C_{B0})^{0.21}}{(C_{C0} + C_{A0}X_A)} \qquad (3.4)$$

Where

K = Rate constant, $2.5X10^{-5}\ e^{(413/T)}$

A = stands for p-xylene

B = stands for CO III

C = stands for MMT

The performance equation from equation 3.2 is

$$\tau_p = C_{A0} \int_0^{X_{Af}} \frac{dX_A}{-r_A} \tag{3.5}$$

Substituting for $-r_A$ in the above equation gives;

$$\tau_p = C_{A0} \int_0^{X_{Af}} \frac{C_{A0}\ (N + X_A)\ dX_A}{K\ C_{A0}^{2}\ (1 - X_A)\ C_{A0}^{0.21}\ (M)^{0.21}} \tag{3.6}$$

Where

$$M = \frac{C_{B0}}{C_{A0}}$$

$$N = \frac{C_{C0}}{C_{A0}}$$

Simplification of the equation gives;

$$\tau_p = \frac{C_{A0}}{C_{A0}^{1.21}\ K} \int_0^{X_{Af}} \frac{dX_A\ (N + X_A)}{(1 - X_A)^2 (M)^{0.21}} \tag{3.7}$$

$$\tau_p = \frac{C_{A0}}{C_{A0}^{1.21}\ K\ M^{0.21}} \int_0^{X_{Af}} \frac{N dX_A}{(1 - X_A)^2} + \frac{X_A dX_A}{(1 - X_A)2} \tag{3.8}$$

Substituting -t for $1 - X_A$ and in the integral gives;

$$\tau_p = \frac{1.0}{C_{A0}^{0.21}\ K\ M^{0.21}} \int \left[\frac{N\ dt}{t^2} + \frac{(t + 1)dt}{t^2} \right] \quad (3.9)$$

Analytical integration yields:

$$\tau_p = \frac{1.0}{C_{A0}^{0.21}\ K\ M^{0.21}} \left[(N + 1)\left[\frac{1.0}{(1 - X_{Af})} - 1.0 \right] + \ln (1 - X_A) \right] \quad (3.10)$$

The above equation determines the residence time needed for a given conversion.

Ideal Mixed Reactor

In an ideal mixed reactor like a CSTR the concentration is uniform throughout the reactor and exits at the bulk concentration. Hence the mass balance becomes simpler and gives the following performance equations, subsequently the rate expression is substituted in equation 3.11 to get the relationship between residence time and conversion.

$$\frac{V}{F_{A0}} = \frac{X_A}{-r_A} = \frac{C_{A0} - C_A}{C_{A0}(-r_A)} \quad (3.11)$$

$$\tau = \frac{V}{v} = \frac{C_{A0}X_A}{-r_A} \quad (3.12)$$

Substituting for $-r_A$ in the above equation gives

$$\tau_c = \frac{C_{A0}X_A\ (C_{C0} + C_{A0}X_A)}{K\ \ C_{A0}{}^2(1 - X_A)^2\ \ (C_{B0})^{0.05}} \qquad (3.13)$$

Sparger

Bubble Size at the Sparger

The bubble diameter is dependent on the equilibrium between surface tension and buoyancy forces [8]. As the air flow rate increases, bubbles leave as a chain from the orifice. At this condition, the diameter of the bubble is dependent on the number of bubbles formed. A simple relation given by Davidson and Harrison [9] can be used to estimate bubble diameter.

$$D_b = 1.17\ U_0{}^{0.4}\ d_0{}^{0.8}\ g^{-0.2} \qquad (3.14)$$

Where

D_b = diameter of the bubble, meters

U_0 = superficial gas velocity, m/s

d_0 = diameter of orifice, meters

g = acceleration due to gravity, 9.81 m/s^2

More complex relations have been established by Kumar et al. [10], but the above equation is adopted for this study. When gas flow rates are increased bubble formation at the sparger becomes unstable. Leibson et al. [11] and Bhavaraju et al. [12] found this transition to occur at $2000 < D_bU_bP/\mu < 10000$.

Bubble Size at a Distance From the Sparger

The bubble formed at the sparger can either coalesce or disperse. In a coalescing media as in this case, the bubble diameter can be estimated using a formula reported by Calderbank [13] and Lee and Meyrick [14].

$$D_b = 4.15 \frac{\sigma^{0.6}}{(P/V)^{0.4} \rho^{0.2}} \epsilon^{0.5} + 9 \times 10^{-4} \quad (3.15)$$

Where

(P/V) = is the work done, Dynes/m^3

σ = surface tension between gas and liquid, N m^{-1}

ρ = density of liquid, kg m^{-3}

ϵ = void fraction

The P/V and ϵ terms cancel approximately each other out.

$$D_b = 4.15 \frac{\sigma^{0.6}}{\rho^{0.2}} + 9 \times 10^{-4} \quad (3.16)$$

and in a noncoalescing media D_b can be calculated according to Lehrer [15] as follows

$$D_b = 1.93 \frac{\sigma^{0.6}}{(P/V)^{0.4} \rho^{0.2}} \quad (3.17)$$

Bubble rise velocity

The bubble rise at a given frequency from the sparger, proceeds like a chain to the top of the reactor. To simplify further, the following assumptions are made

1. The velocity of the bubble is directly proportional to the diameter of the bubble.
2. Interaction of the bubble swarm gives rise to bigger sized bubbles.
3. Wall effects are neglected.

With the above mentioned assumptions, the rate of rise of the bubble was found by Davidson and Harrison [9] to be:

$$U_{br} = 0.711\ (gD_b)^{\frac{1}{2}} \qquad (3.18)$$

Where

g = acceleration due to gravity, cm/sec^2

D_b = diameter of bubble, cm

U_{br} = bubble rise velocity, cm/sec

The absolute rise velocity of the bubble is given by:

$$U_b = (U_0 - U_{mf}) + U_{br} \qquad (3.19)$$

Where

U_0 = superficial gas velocity, cm/s

U_{mf} = minimum fluidizing velocity, cm/s

Liquid Mixing and Mass Transfer Coefficient

Liquid mixing in a bubble column is due to several processes. The bubbles themselves contribute to mixing because of the liquid transport due to the velocity differences around the bubble. The following equations are suggested by Davidson and Harrison [9].

$$V_l^c = 2.7\ (g\ U_0\ )^{1/3} \qquad (3.20)$$

$$\phi_l = 0.3(D_{bed})^{5/3}(V_g g)^{0.33} \qquad (3.21)$$

where

V_l^c = liquid velocity, m/s

ϕ_l = liquid mixing, m3/s

D_{bed} = diameter of bed, m

V_g = velocity of gas, m/s

Relationship Between Bubble Phase Variables

On a superficial velocity basis, the total flow and that through the two phase region as given by Kunii et al. [16] as:

$$U_b = (1 - \delta)U_{mf} + \delta(U_b + 3U_{mf}) \qquad (3.22)$$

In a bed of large bubbles, each rising bubble carries liquid up the bed. The upward velocity of the liquid is then simply that of the bubble itself, or:

$$U_b = (1 - \delta)U_{mf} + \delta U_b \qquad (3.23)$$

therefore;

$$U_b = \frac{U_b - (1 - \delta)U_{mf}}{\delta} \approx \frac{U_0 - U_{mf}}{\delta} \qquad (3.24)$$

where

δ = is the fraction of bed consisting of bubbles.

Interphase Coefficients

To determine the mass transfer characteristics it is essential to consider the interchange between bubbles and the bubble cloud. This consists of flow across a phase

boundary and mass transport between the bubble and the liquid. The mass transfer between the bubble and the liquid is given by Kunii et al.[16] as:

$$K_{bc} = 4.5 \frac{U_{mf}}{D_b} + 5.85 \frac{D_{AB}^{1/2} g^{1/4}}{D_b^{5/4}} \quad (3.25)$$

where

K_{bc} = mass transfer coefficient between bubble and cloud, s^{-1}

D_{AB} = diffusion coefficient between catalyst and p-xylene, cm^2/s

The mass transfer between the cloud and the emulsion is given by Kunii et al. [16] as:

$$K_{ce} \approx 6.78 \left[\frac{\epsilon_{mf} D_{AB} U_b}{D_b^3} \right]^{1/2} \quad (3.26)$$

where

K_{ce} = mass transfer coefficient between cloud and emulsion, s^{-1}

ϵ_{mf} = void fraction in a bed at minimum fluidizing conditions

The ratio of solids (catalyst and residue) dispersed in the bubble to the volume of bubbles in the bed, τ_b, is given by Kunii et al. [16] as:

$$\tau_b = \frac{(1 - \epsilon_{mf})(1 - \delta) m_b}{\delta} \quad (3.27)$$

where

m_b = fraction of solids in bubble

Similarly, the ratio of the solids in the cloud to the volume of bubbles in the bed, τ_c, is given by:

$$\tau_c = (1 - \epsilon_{ms}) \left[\frac{3U_{mf}/\epsilon_{mf}}{0.711(gD_b)^{\frac{1}{2}} - U_{mf}/\epsilon_{mf}} + \frac{V_w}{V_b} \right] \qquad (3.28)$$

where

V_w = volume of wake following a gas bubble, cm^3

V_b = volume of gas bubble, cm^3

The ratio of solids in the emulsion to the volume of bubbles in the bed, τ_e, is given by:

$$\delta(\tau_b + \tau_c + \tau_e) = (1 - \epsilon_{mf})(1 - \delta) \qquad (3.29)$$

Assuming that the flow pattern in the bed for downflow of emulsion is as illustrated in Figure 3., i.e., the liquid that is carried long with the bubble moves downward after the bubble disintegrates, an accounting for p-xylene in the cloud, emulsion and in the bubble was given by Kunii et al. [16] as:

$$K_f = \frac{L_f K_r}{U_b} \left[\tau_b + \cfrac{1}{K_r/K_{bc} + \cfrac{1}{\tau_c + \cfrac{1}{K_r/K_{ce} + 1/\tau_e}}} \right]$$

where

K_f = 1st order reaction rate group for fluidized bed.

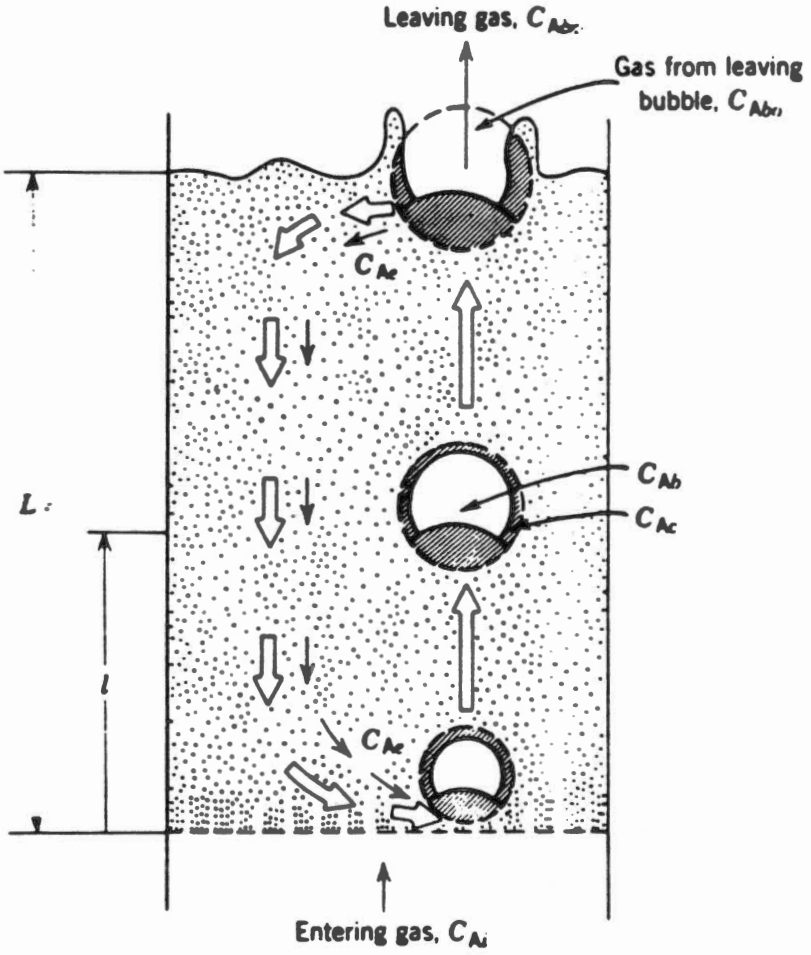


Figure 3. Bubble rise and circulation pattern; adapted from Kunii and et al. [16]

L_f = is the length of the reactor, m

K_r = 1st order rate constant, s^{-1}

τ_b = ratio of solids in bubbles to volume of bubble

τ_c = ratio of solids in clouds to volume of bubble

τ_e = ratio of solids in emulsion to volume of bubble

K_{bc} = mass transfer coefficient between bubble and cloud, s^{-1}

K_{ce} = mass transfer coefficient between cloud and emulsion, s^{-1}

U_b = bubble rise velocity, m/s

By definition the conversion of p-xylene is given by:

$$X_A = \frac{C_{A0} - C_{Af}}{C_{A0}} \tag{3.31}$$

or

$$\frac{C_{Af}}{C_{A0}} = 1 - X_A \tag{3.32}$$

Assuming a pseudo first order irreversible reaction

$$K\tau = -\ln(1 - X_A) \tag{3.33}$$

Making the substitution of K_f for $K\tau$ gives:

$$K_f = -\ln(1 - X_A) \tag{3.34}$$

CHAPTER IV

PROBLEM STATEMENT AND APPROACH

The purpose of this thesis is to develop a model to simulate a sparger reactor. Sparger reactors, as discussed earlier, deviate from ideal plug flow reactor behavior to a great extent. To start with, the variables: namely temperature, pressure, initial moles of reactants and catalyst, diameter of the orifice, number of orifices, diameter of heat exchanger tubes, and pitch on a triangular layout, are specified.

Sparger reactors typically have reactants entering the reactor at low flow rates. It is difficult to model the system at steady state because of the entrance effects and the resulting change in concentration. In this preliminary work the reactor is modeled as a reactor operating at pseudo-steady state with no external input or output streams. However, internal circulation in the reactor due to the bubble rise and the wake that rises along with the bubble must be included. The following assumptions were made to simplify the problem and calculations.

1. The reactor is assumed to have no input or output streams.

2. The catalyst is uniformly distributed in the reactor.
3. The core of the reactor that is not occupied by tubes acts like a plug flow channel (hatched section in figure 4.)
4. The other portions of the reactor are well mixed, and behaves like a batch reactor (Figure 4.)
5. The reactor is at psuedo-steady state.
6. The reaction takes place at constant temperature.

In this idealized reactor, the concentration of the reactants is not the same through out. The plug flow channel section can be visualized as a separate reactor operating at steady state, where the inlet and exit streams flow from and into the well mixed portion of the reactor. This is assumed to be true for each cycle (time taken for bubble to reach top of the reactor), and the change in concentration for the inlet and exit streams is neglected due to the short time duration for each cycle, i.e., the fluid surrounding the plug flow core is well mixed and no chemical reaction is assumed to occur in this region.

The assumption that the reactor has no external circulation, has certain drawbacks. The total time in the reactor is fixed, hence the residence time for the plug flow reactor section has to be defined. The time taken for the bubble to reach the top of the reactor, is taken as one cycle. Since the air circulation rate is high, the

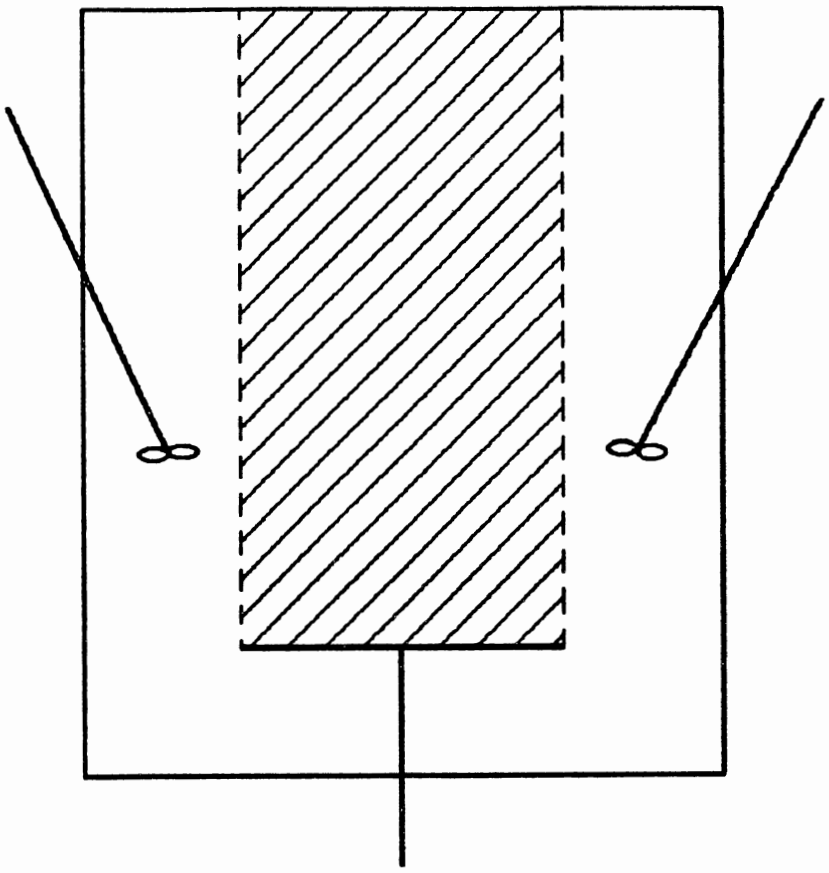


Figure 4. Representation of Reactor Configuration as used in model.

bubbles tend to force up all the liquid in this section, and liquid velocity assumes the bubble rise velocity. The plug flow section volume is known or estimated and thus volumetric flow rate can be calculated. This fixes the residence time for one cycle in the plug flow channel. The model is treated as a steady state reactor for one cycle and the concentrations at the top and bottom of the plug flow channel are determined. The concentration of the well mixed portion is taken as the average of these two concentrations, and oxygen concentration is attributed mainly to the bubbles that move downward. The same residence time is used as the space time in the well mixed section. At the end of each cycle the concentrations are averaged on a volumetric basis, and the next cycle is restarted with the new bulk concentration.

The program organization is indicated in Figure 5. With the input conditions fixed, the following steps were adopted in developing the model

1. the subroutine INITIAL fixes the dimension of the reactor based on the inlet conditions.
2. the subroutine INITIAL also calculates the bubble diameter, rise velocity, and other bubble characteristics.
3. the subroutine PCVOL initializes the plug flow section from the well mixed section.
4. the subroutine FINAL calculates the overall conversion.

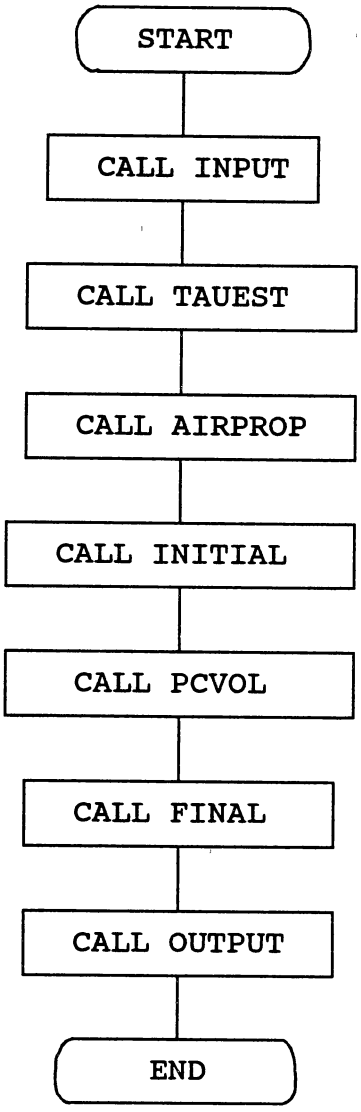


Figure 5. Program organization for the model.

Description of the Subroutines

INPUT

This subroutine developed using EZVU allows the user to change the variables on screen. This allows the user to test the model by changing one or more of the variables.

TAUEST

This subroutine is used to estimate the conversion for a given residence time. The equations discussed in the previous section are used in this subroutine. This reactor behaves both as a plug flow reactor and as a batch reactor, the average of the conversion from both cases provides the estimate for the overall conversion. This subroutine is used in initializing the reactor dimensions.

AIRPROP

This subroutine calculates the properties of air at the input conditions specified.

INITIAL

This subroutine is used to initialize the size of the reactor. The diameter of the reactor is fixed based on the amount of p-xylene initially present in the reactor. The diameter of the bubble is calculated from a knowledge

of the flow rate of air required from the following equation

$$D_b = 1.17\ U_0^{0.4}\ d_0^{0.8}\ g^{-0.2}$$

where

U_0 = superficial gas velocity, m/s

d_0 = diameter of orifice, m

g = acceleration due to gravity, 9.81 m/s^2

The bubble rise velocity in the reactor is determined using the equation given below

$$U_{br} = 0.711\ (gD_b)^{\frac{1}{2}}$$

Where

g = acceleration due to gravity, cm/sec^2

D_b = diameter of bubble, cm

U_{br} = bubble rise velocity, cm/s

Subroutine TAUEST is used to estimate the conversion as discussed earlier. This estimate for the conversion is needed to calculate the number of heat exchanger tubes and the length of the reactor. The number of heat exchanger tubes is calculated in the following manner.

$$\text{Total heat removed} = N_{A0}X_A(\triangle H_R)$$

where

N_{A0} = initial moles of p-xylene in the reactor, Kgmoles

X_A = conversion of p-xylene

$\triangle H_R$ = heat of reaction, cal/Kgmole

$$\text{Heat transfer area} = \frac{\text{Total heat removed}}{U(\triangle T)}$$

where

U = overall heat transfer coefficient, cal/hr cm^2 °C

$$\text{Number of tubes needed} = \frac{\text{Heat Transfer area}}{\text{Area per tube}}$$

PCVOL

This subroutine is used to determine the radius of the core that behaves as a plug flow reactor. The reactor dealt with here is not symmetrical, i.e. the tubes are not placed throughout the radius. The number of tubes that can be placed in the arc of length rθ, can be calculated. The radius of the next inner ring is calculated and the procedure is repeated until the total number that can be fitted equals the actual number of tubes needed.

FINAL

This subroutine is employed to calculate the final conversion in the reactor. The reactor is divided into segments each having a length 400 centimeters. From the bubble rise velocity, the time in each segment is calculated. From this residence time the conversion is calculated using subroutine TAUVSXA. The velocity of the bubble changes due to bubble growth and other factors. Hence the residence time in each segment is different. The total time required for the bubble to reach the top of the reactor is taken as the space time in the well mixed portion of the reactor. The concentration is averaged on

a volumetric basis after each cycle. The procedure is repeated until the total residence time in the reactor equals the specified time duration. The source code for this model is listed in the appendices. IBM software EZVU was used to simulate the control panels. This software makes the model very friendly.

Testing

The validation of the model is difficult due to the lack of experimental data available in the literature. However, the model was tested to study the effect on conversion of the following variables.

1. temperature,
2. pressure,
3. cobalt concentration, and
4. time.

Effect of Temperature

The model was tested for sensitivity with temperature with all other variables remaining constant. To prevent side reactions, it is preferable to operate the reactor between 140 and 170 °C. To study the effect of temperature on the system, the following trials were performed.

The following operating conditions were used as inputs:

1. isothermal reaction
2. operating temperature = 140 - 170°C in two degree increments
3. system pressure = 6 ATM
4. initial moles of p-xylene = 6000 Kgmoles
5. initial moles of cobalt catalyst = 60 Kgmoles
6. initial moles of MMT = 100 Kgmoles
7. total time in reactor = 1 hour

The final conversion of p-xylene from the model was found to be 29.5% at 140°C. There are no experimental data, to confirm this result, but the conversion level is reasonable compared to typical industrial conversion levels.

When the temperature was increased to 150°C, the final conversion of p-xylene from the model was found to be 28.6%. So, for a increase of 10°C the conversion decreased by roughly 1%. The results are listed in Table I.

Figure 6. shows the predictions from the model for the change in temperature on the conversion of p-xylene. It is seen that the conversion of p-xylene can be controlled by the oxidation temperature, although many other factors can affect it. It can also be seen that the % MMT yield increases with lower oxidation temperature. This effect can be attributed to the exothermic nature of the reaction.

TABLE I

EFFECT OF TEMPERATURE ON CONVERSION

Trial Number	Temperature °C	Pressure Atmospheres	Conversion from model (%)
1.	140.0	6.0	29.5
2.	142.0	6.0	29.4
3.	144.0	6.0	28.9
4.	146.0	6.0	28.8
5.	148.0	6.0	28.7
6.	150.0	6.0	28.6
7.	152.0	6.0	28.5
8.	154.0	6.0	28.0
9.	156.0	6.0	27.9
10.	158.0	6.0	27.8
11.	160.0	6.0	27.7
12.	162.0	6.0	27.2
13.	164.0	6.0	27.1
14.	166.0	6.0	27.0
15.	168.0	6.0	26.9
16.	170.0	6.0	26.8

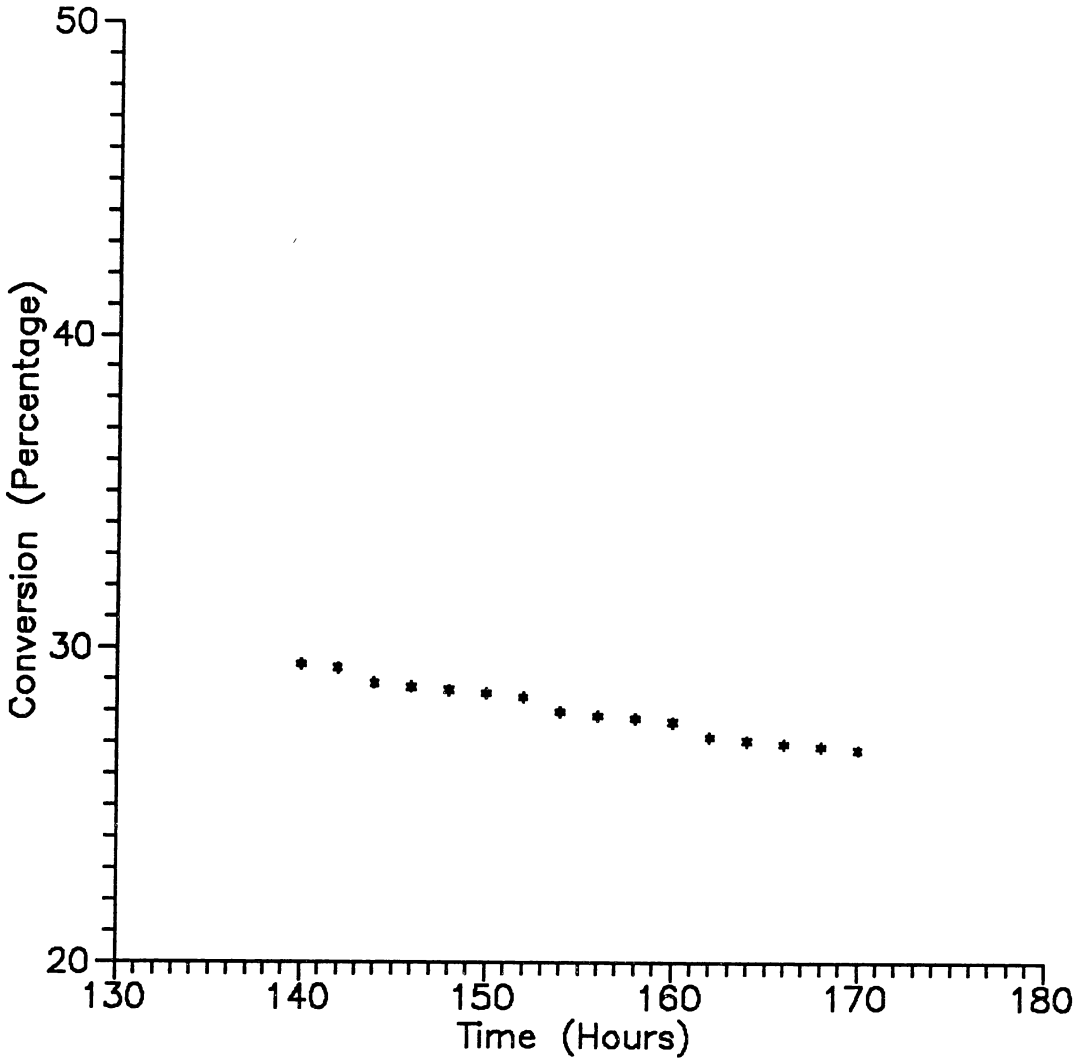


Figure 6. Temperature vs Conversion

Effect of Pressure

The operating pressure for the reaction is typically between 4 and 8 atmospheres in normal industrial operation. The model was tested for pressures in this range. The results and discussion are given below.

1. isothermal reaction
2. operating temperature = 140 °C
3. system pressure = 4 - 7 ATM in steps of 0.3
4. initial moles of p-xylene = 6000 Kgmoles
5. initial moles of cobalt catalyst = 60 Kgmoles
6. initial moles of MMT = 100 Kgmoles
7. total time in reactor = 1 hour

The conversion of p-xylene was found to be 33.6% at 4 atmospheres. This conversion is slightly lower than that for an ideal plug flow reactor.

When the pressure is increased to 5.5 atmospheres, the conversion from the model was found to be 30.2%. The conversion decreases as the pressure is increased. For an increase of operating pressure of 1.5 atmospheres the conversion decreases by roughly 3.0%. The results are given in Table II.

The effect of pressure on the conversion of p-xylene as predicted from the model is represented in Figure 7. It is seen that the oxidizer pressure can also affect the production rate. The pressure of the system controls the size of the air bubbles. When the bubbles are larger

TABLE II

EFFECT OF PRESSURE ON CONVERSION

Trial Number	Temperature °C	Pressure Atmospheres	Conversion from model (%)
1.	140.0	4.0	33.6
2.	140.0	4.3	32.9
3.	140.0	4.6	31.9
4.	140.0	4.9	31.3
5.	140.0	5.2	30.8
6.	140.0	5.5	30.2
7.	140.0	5.8	29.6
8.	140.0	6.1	29.4
9.	140.0	6.4	29.2
10.	140.0	6.7	29.2
11.	140.0	7.0	29.1

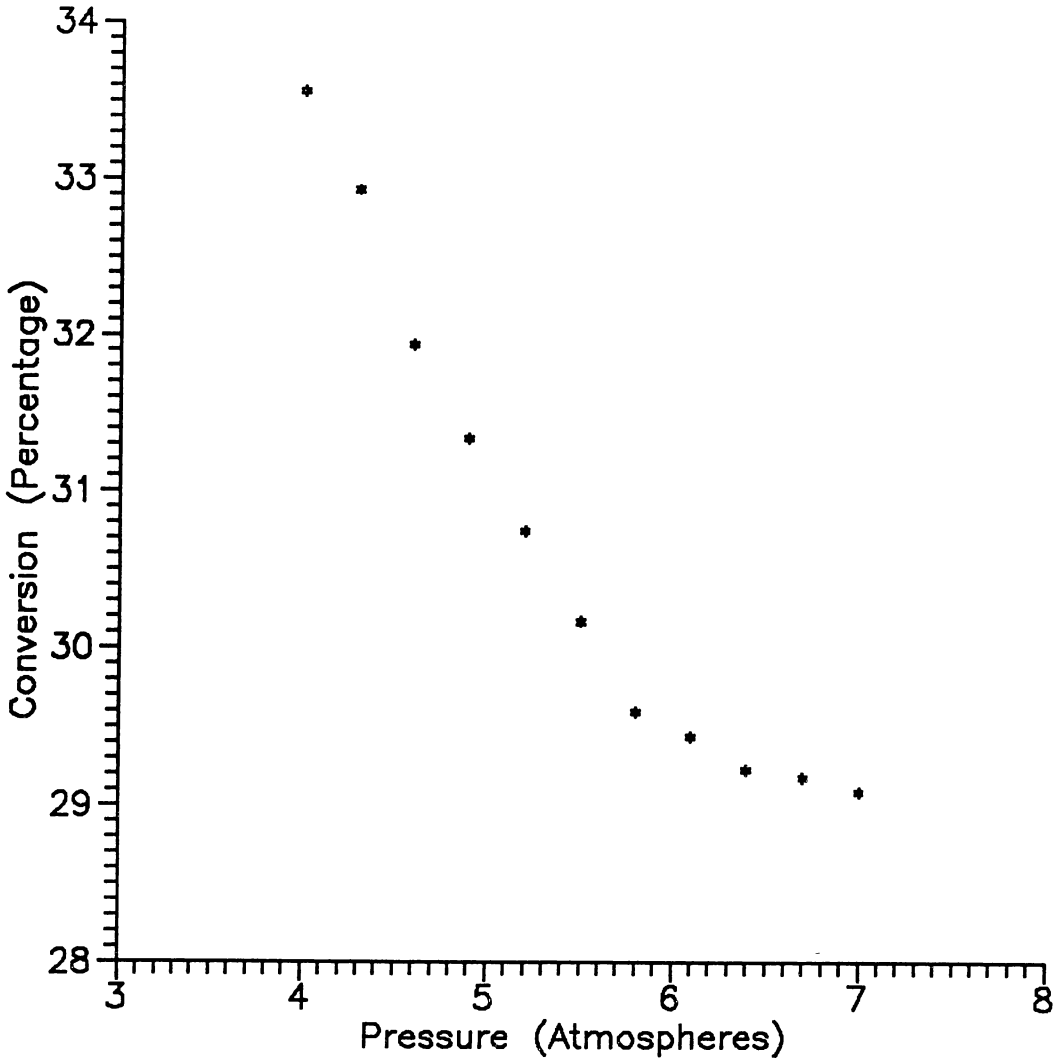


Figure 7. Pressure vs Conversion

in size, the circulation is higher, and the surface area is lowered, hence the conversion decreases.

Effect of Cobalt Concentration

The effect of cobalt concentration on the reaction should be significant as seen from the rate expression for the reaction. Trials were performed on the model to study the effect of the cobalt concentration on the reaction, at the following conditions.

1. isothermal reaction
2. operating temperature = 140 °C
3. system pressure = 6 ATM
4. initial moles of p-xylene = 6000 Kgmoles
5. initial moles of cobalt catalyst = 20 - 200 Kgmoles in steps of 20
6. initial moles of MMT = 100 Kgmoles
7. total time in reactor = 1 hour

The prediction from the model was found to be 29.1% for an initial moles of cobalt of 20 Kgmoles. Similar trials were conducted on the model, at different concentration levels. The predictions from the are given in Table 3. The conversion doesn't vary when the cobalt concentration is increased, as indicated in Figure 8. However, at very low cobalt concentration levels, p-xylene gets decomposed into CO_2 and water.

TABLE III

EFFECT OF COBALT CONCENTRATION ON CONVERSION

Trial Number	Initial moles of cobalt (Kgmoles)	Initial moles of p-xylene	Conversion from model (%)
1.	20.0	6000.0	29.1
2.	40.0	6000.0	29.5
3.	60.0	6000.0	29.5
4.	80.0	6000.0	31.5
5.	100.0	6000.0	33.3
6.	120.0	6000.0	33.5
7.	140.0	6000.0	33.5
8.	160.0	6000.0	33.5
9.	180.0	6000.0	33.6
10.	200.0	6000.0	33.6

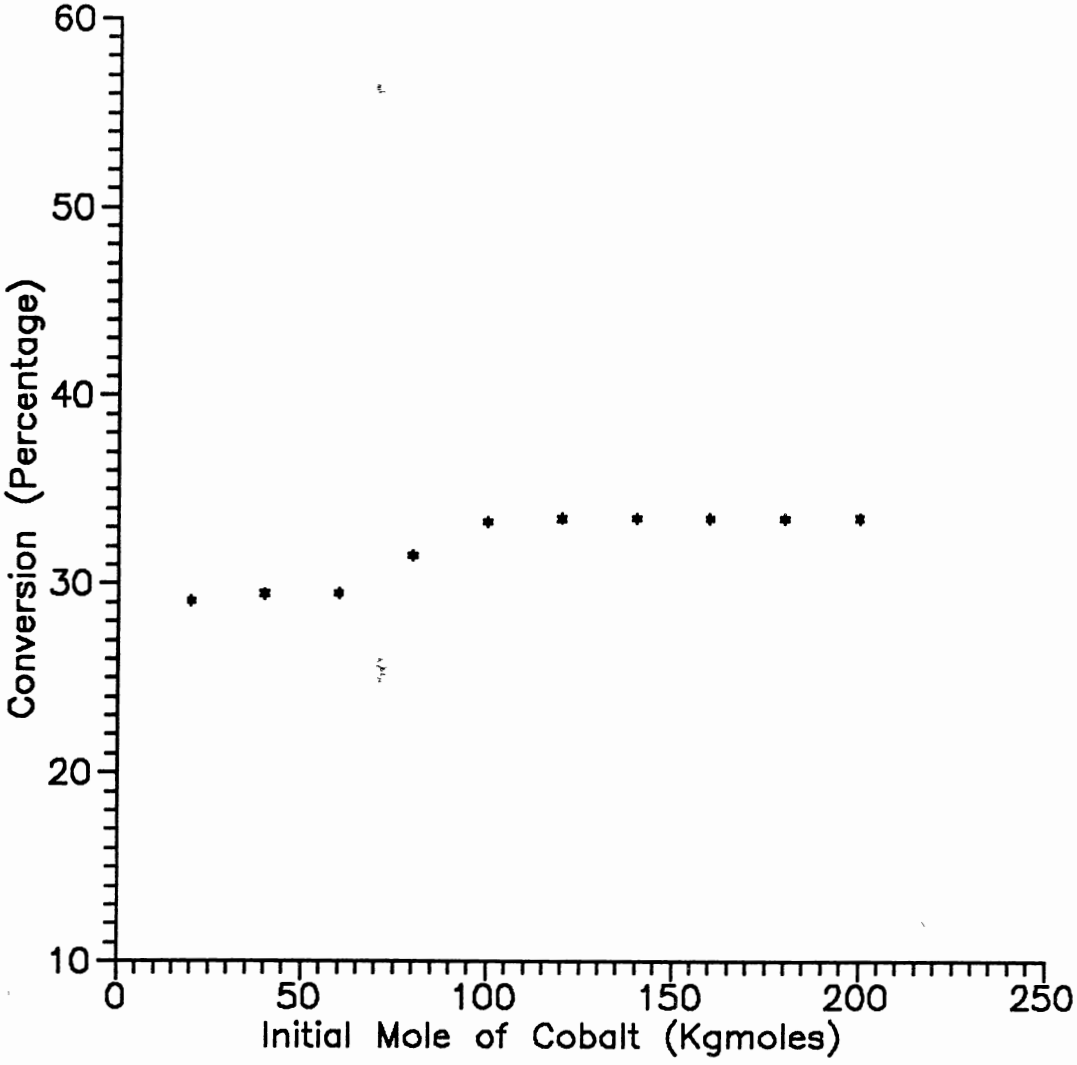


Figure 8. Cobalt Concentration vs Conversion

Effect of Total Time in Reactor

The total time in the reactor has a significant effect on the rate of the reaction, so time versus conversion is an important criteria. To obtain an idea about the reaction rate as a function of time the following trials were performed at the given conditions.

1. isothermal reaction
2. operating temperature = 140 °C
3. system pressure = 6 ATM
4. initial moles of p-xylene = 6000 Kgmoles
5. initial moles of cobalt catalyst = 60 Kgmoles
6. initial moles of MMT = 100 Kgmoles
7. total time in reactor = 1-10 hours in steps of 1.

For the initial case, the model predicted a conversion of 29.5%. Similar trials were carried out by incrementing the time in the reactor. The results are listed in Table IV. The conversion increases as the time allowed in the reactor is increased. The reaction is fast for the first few hours in the reactor, but as the amount of MMT formed increases, the reaction gets retarded. The effect of total time in reactor, on the conversion as predicted from the model plotted in Figure 9.

TABLE IV

EFFECT OF TIME ON CONVERSION

Trial Number	Total time in reactor (hours)	Temperature °C	Conversion from model (%)
1.	1.0	140.0	29.5
2.	2.0	140.0	50.8
3.	3.0	140.0	58.3
4.	4.0	140.0	69.3
5.	5.0	140.0	71.3
6.	6.0	140.0	76.8
7.	7.0	140.0	81.4
8.	8.0	140.0	82.1
9.	9.0	140.0	83.3
10.	10.0	140.0	86.1

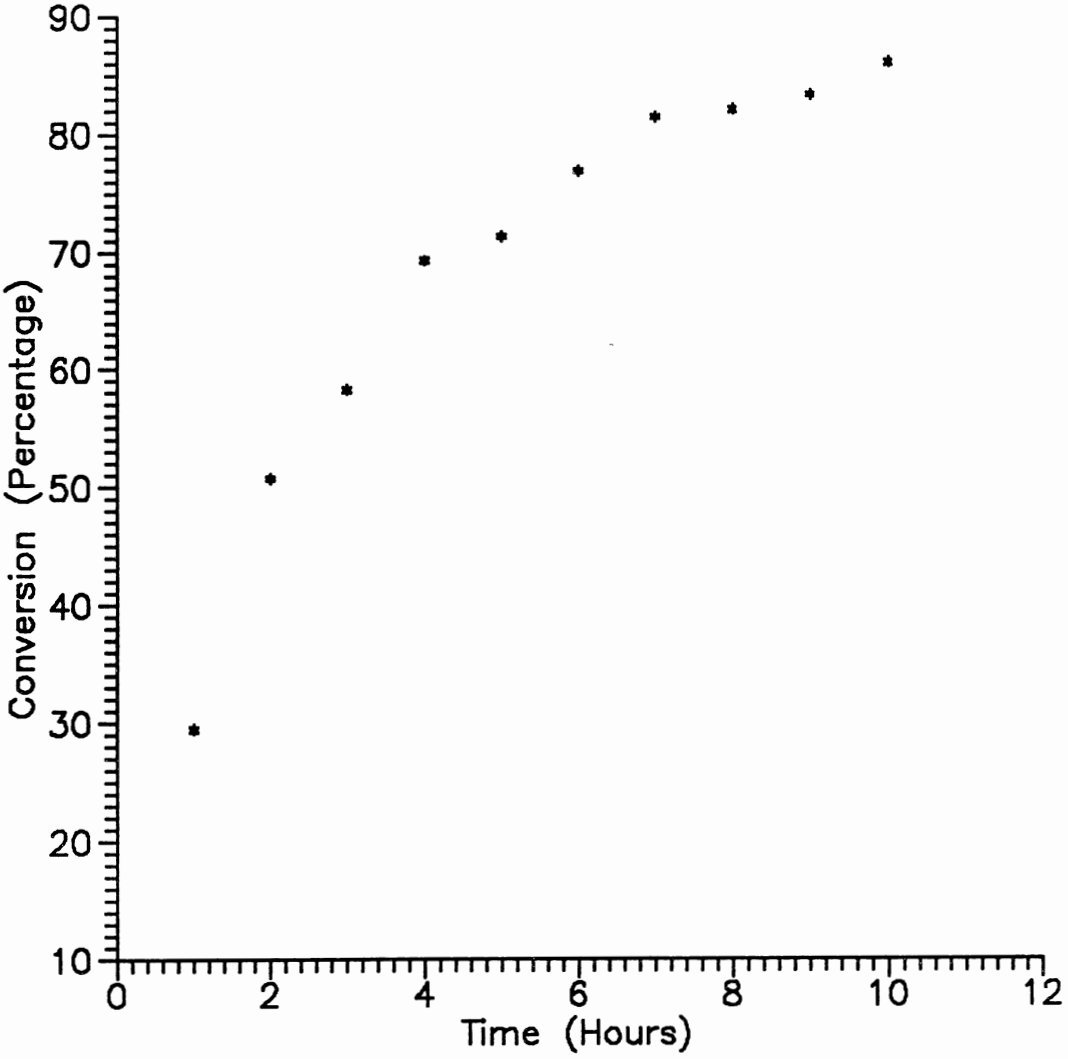


Figure 9. Time vs Conversion

CHAPTER V

CONCLUSIONS AND RECOMMENDATIONS

The purpose of this study was to simulate a sparger reactor for the oxidation of p-xylene. This model perdicts conversion for changes in

1. operating temperature,
2. operating pressure,
3. initial concentration of reactants, and
4. residence time in the reactor.

Conclusions

In this study several conclusions can be made from the model output data. The major conclusions are

1. Pressure has an indirect effect on the conversion by affecting the bubble characteristics.
2. The reaction is insensitive to the concentration of the catalyst.
3. The air circulation rate is so high, i.e. three moles of air is circulated per mole of p-xylene in the reactor, so the liquid velocity assumes the velocity of the rising gas in the plug flow core of the reactor.

Recommendations

1. The ideal gas law was used in the reactor model to evaluate concentrations. A study on the gas behavior, could suggest a better equation of state.
2. This study did not consider any reversible reactions, which are prominent at high concentrations of MMT and occur at conversions greater than 50%. Hence it is suggested that these considerations be used in future work to more accurately model the process.
3. It is recommended that additional experimental data be obtained to validate the model. This model cannot be generalized or calibrated until additional kinetic data is generated for specific catalysts.
4. Side reactions have to considered to model the system accurately and to compare with any industrial data.

REFERENCES

1. Kanazawa, M.; in Tannenbaum, S. R.; Wang, D. I. C. Single Cell Protein II. Cambridge: Massachesetts Institute of Technology Press; 1975.

2. Klingman; "Method for Oxidation of P-xylene and Method for Preparing Dimethylterephthlate"; 4342876 (U. S. Patent); 1982.

3. Pandit, A. B.; Joshi, J. B.; "Mass nd Heat Transfer Characteristics of Three Phase Sparged Reactors" Chemical Engineering Res. Des.; 1986; 64(125).

4. Baerns et al.; "Method for Manufacturing of Monomethyl Terephthalate"; 3923867 (U. S. Patent); 1975.

5. Hronec, M.; Cvengrosova, Z.; IIavsky, J."Kinetics and Mechanism of Cobalt Catalyzed Oxidation of P-xylene in the Presence of Water"; Industrial Engineering Chemical Process Des. Dev.; 1985; 24: 787 - 794.

6. Klingman; "Liquid Phase Oxidation of P-xylene"; 4442972 (U. S. Patent); 1974.

7. Baerns et al.; "Contacting Apparatus for Oxidation of P-xylene"; 4124824 (U. S. Patent); 1978.

8. Ruff, K.; Pilhofer Th.; Mersmann, A. "Liqiud Entrainment in Sparged Reactors"; Chemical Ing. Technology; 1976; 48: 759 - 764.

9. Davidson, J. K. Fluidized particles. London: Cambridge University Press; 1963.

10. Kumar, A.; Degaleesan T. W.; Laddha, G. S. "Bubble Characteristics in Three Phase Reactors"; Canadian Journal of Chemical Engineering; 1976; 54:503 -508.

11. Liebson, I.; Holcomb, E. G.; Cacoso, A. G.; Jacmic, J. J. "Effect of Circulation on Heat and Mass Transfer in Sparged Reactors"; AICHE Journal; 1956; 2: 296 -306.

12. Bhavaraju, S. M.; Russell, T. W. F.; Blanch, H. W "Transition Flow in Three Phase Sparged Reactors"; AICHE Journal; 1978; 24: 454 -466.

13. Calderbank, P. H. "Mass Transfer, Mixing and Heat Transfer in Low Viscosity Bubble Column Reactors"; Trans. Inst. Chem. Eng.; 1958; 36: 443 -463.

14. Lee, J. C.; Meyrick, D. L. "Fluidization in Three Phase Reactors"; Trans Inst. Chem. Eng.; 1970; 48: T37.

15. Lehrer, I. H. "Flow Paterns of Gas Through Fluidized Beds" Industrial Engineering Chemistry Process Des. Dev.; 1971; 10: 37 - 40.

16. Kunii, D.; Levenspiel, O. Fluidization Engineering. London: John Wiley and Sons, Inc.; 1969.

APPENDICES

APPENDIX A

PROGRAM LISTING FOR MAIN

```
DEBUG

$STORAGE:2
        DIMENSION R(100)

C   Model for sparger reactor used in the  manu-
C   facture of Dimethyl terephthalate.  This
C   program designs a reactor to handle the input
C   requirements and proceeds to calculate the
C   expected conversion based on the design and
C   other criteria.

        INTEGER RC


        COMMON /Z1/ XA,TEMP,PRESS,PITCH,DHE
        COMMON /Z2/ TAUA,ANA0,ANB0,ANC0
        COMMON /Z3/ DOR,ANOR,DB,DBED,ALF,AKL
        COMMON /Z4/ VELBR,VELB,PHIL,NTA,U
        COMMON /Z5/ DELTA,TI,TC,NI,NU,RPFR
        COMMON /Z6/ XAA,DELHR,U0,AMDOT,TOUT,TIN
        COMMON /Z7/ DENG,TCG,VISG,GASCP,PRANG,DAB
        COMMON /Z8/ RATEK,CATDIA,CATDEN,EPSMF,VMF,EPSM,CATCP,DELTAT


        OPEN(7,FILE='VEN.OUT',STATUS='UNKNOWN')

C
C       Defining the variables a value as default
C
C

C*******************************************************
C                   NOMENCLATURE USED
C
C*******************************************************
C        ANA0=INITIAL MOLES OF P-XYLENE Kg-Moles
C        ANB0=INITIAL MOLES OF COBALT CATALYST Kg-Moles
C        ANC0=INITIAL MOLES OF PMT Kg-Moles
C        TEMP=TEMPERATURE DEGREE CELCIUS
C        PRESS=PRESSURE IN ATMOSPHERES
C        TIN=INLET TEMPERATURE OF COLD STREAM
C        DOR=DIAMETER OF ORIFICE CENTIMETER
C        ANOR=NUMBER OF ORIFICES
C        DELTA=LENGTH INCREMENT IN CENTIMETERS
C        U0=GAS SUPERFICIAL VELOCITY CM/SEC
C        DHE=DIAMETER OF HEAT EXCHANGER TUBES CENTIMETERS
C        PITCH=PITCH OF TUBES ON A TRIANGULAR LAYOUT CENTIMETERS
C        CATDIA=DIAMETER OF CATALYST METERS
C        CATDEN=DENSITY OF CATALYST GRAM/CC
C        CATCP=SPECIFIC HEAT OF CATALYST
C        PRANG=PRANDTL NUMBER FOR AIR
C        DAB=DIFFUSION COEFFICIENT CM SQUARE/SEC
C*******************************************************
```

```
        RC=0
        ANA0=6000
        ANB0=600
        ANC0=10
        TEMP=140.0
        PRESS=6.0
        TIN=80.0
        DOR=0.2
        ANOR=500
        DELTA=400.0
        U0=25
        DHE=3.25
        PITCH=7.0
        CATDIA=51.E-4
        CATDEN=2.5
        EPSM=0.5
        VMF=0.2
        EPSMF=0.6
        CATCP=0.2
        PRANG=0.77
        DAB=0.39 C
C     THIS SUBROUTINE EXITS TO DOS AND EXECUTES PROGRAM START
C     AND RETURNS BACK TO THIS POINT AT THE END OF PROGRAM START
C

      call ispff(9,'run start',rc)

C
C     This is part of EZVU facility used to initialize variables
C     for the input and output screens
C


      call ispffv(5,'XA f5',rc,XA,4)
      call ispffv(7,'TEMP F5',rc,TEMP,4)
      CALL ISPFFV(8,'PRESS F3',RC,PRESS,4)
      call ispffv(6,'DHE f4',rc,DHE,4)
      CALL ISPFFV(8,'PITCH F3',RC,PITCH,4)

      CALL ISPFFV(6,'DOR F3',RC,DOR,4)
      CALL ISPFFV(7,'ANOR F2',RC,ANOR,4)
      CALL ISPFFV(8,'DELTA F3',RC,DELTA,4)
      CALL ISPFFV(5,'U0 F3',RC,U0,4)
      call ispffv(7,'ANA0 F2',rc,ANA0,4)

      call ispffv(7,'ANB0 F2',rc,ANB0,4)
      CALL ISPFFV(7,'ANC0 F2',RC,ANC0,4)
      call ispffv(9,'CATDIA f4',rc,CATDIA,4)
      CALL ISPFFV(9,'CATDEN F3',RC,CATDEN,4)
      call ispffv(8,'CATCP f3',rc,CATCP,4)
      call ispffv(7,'EPSM F5',rc,EPSM,4)
      CALL ISPFFV(8,'EPSMF F3',RC,EPSMF,4)
      call ispffv(6,'VMF f4',rc,VMF,4)
      CALL ISPFFV(6,'DAB F3',RC,DAB,4)
```

```
      CALL ISPFFV(7,'PHIL F3',RC,PHIL,4)

      CALL ISPFFV(6,'TIN F2',RC,TIN,4)
      CALL ISPFFV(7,'TOUT F2',RC,TOUT,4)
      CALL ISPFFV(8,'AMDOT F2',RC,AMDOT,4)
      call ispffv(6,'ALT f5',rc,ALT,4)
      call ispffv(7,'TAUA F3',rc,TAUA,4)

      CALL ISPFFV(7,'ABED F3',RC,ABED,4)
      call ispffv(5,'db f4',rc,db,4)
      CALL ISPFFV(6,'Ant F3',RC,ANT,4)
      CALL ISPFFV(6,'AKL F5',RC,AKL,4)
      CALL ISPFFV(4,'U F8',RC,U,4)

      CALL ISPFFV(8,'AVELB F5',RC,AVELB,4)
      CALL ISPFFV(7,'ANA0 F4',RC,ANA0,4)
      CALL ISPFFV(7,'ANC0 F4',RC,ANC0,4)
      CALL ISPFFV(7,'ANAF F4',RC,ANAF,4)
      CALL ISPFFV(7,'ANCF F4',RC,ANCF,4)

      CALL ISPFFV(9,'DELTAT F4',RC,DELTAT,4)
      CALL ISPFFV(6,'XAA F4',RC,XAA,4)

C
C      This subroutine of EZVU puts the variables to the shared
C      pool.
C

      CALL ISPFF(11,'VPUT TEMP S',RC)
      CALL ISPFF(12,'VPUT PRESS S',RC)
      CALL ISPFF(11,'VPUT TAUA S',RC)
      CALL ISPFF(10,'VPUT DOR S',RC)
      CALL ISPFF(11,'VPUT ANOR S',RC)
      CALL ISPFF(12,'VPUT DELTA S',RC)
      CALL ISPFF(9,'VPUT U0 S',RC)
      CALL ISPFF(11,'VPUT ANA0 S',RC)
      CALL ISPFF(11,'VPUT ANB0 S',RC)
      CALL ISPFF(11,'VPUT ANC0 S',RC)

      CALL ISPFF(13,'VPUT CATDIA S',RC)
      CALL ISPFF(13,'VPUT CATDEN S',RC)
      CALL ISPFF(12,'VPUT CATCP S',RC)
      CALL ISPFF(11,'VPUT EPSM S',RC)
      CALL ISPFF(12,'VPUT EPSMF S',RC)
      CALL ISPFF(10,'VPUT VMS S',RC)
      CALL ISPFF(10,'VPUT DAB S',RC)
      CALL ISPFF(11,'VPUT PHIL S',RC)
      CALL ISPFF(11,'VPUT TOUT S',RC)
      CALL ISPFF(10,'VPUT TIN S',RC)


      CALL ISPFF(12,'VPUT AMDOT S',RC)
      CALL ISPFF(11,'VPUT ATAU S',RC)
      CALL ISPFF(10,'VPUT ALT S',RC)
```

```
      CALL ISPFF(10,'VPUT NTA S',RC)
      CALL ISPFF(11,'VPUT ABED S',RC)

      CALL ISPFF(9,'VPUT DB S',RC)
      CALL ISPFF(10,'VPUT AKL S',RC)
      CALL ISPFF(8,'VPUT U S',RC)
      CALL ISPFF(12,'VPUT AVELB S',RC)
      CALL ISPFF(11,'VPUT ANA0 S',RC)

      CALL ISPFF(11,'VPUT ANC0 S',RC)
      CALL ISPFF(11,'VPUT ANAF S',RC)
      CALL ISPFF(11,'VPUT ANCF S',RC)
      CALL ISPFF(10,'VPUT XAA S',RC)
      CALL ISPFF(13,'VPUT DELTAT S',RC)

C
C                SET FUNCTION KEYS
c       CALL ISPFFV(6,'ZF01 C',RC,ZF01,8)
c       CALL ISPFFV(6,'ZF02 C',RC,ZF02,8)
c       CALL ISPFFV(6,'ZF03 C',RC,ZF03,8)
c       CALL ISPFFV(6,'ZF04 C',RC,ZF04,8)
c       CALL ISPFFV(6,'ZCMD C',RC,ZCMD,8)
C                SET INITIAL VALUES OF
C                    FUNCTION KEY

C
C        Define function keys. for the input and output screens.
C

 171    ZF10='QUIT'
        ZCMD='    '
        ZATR='WRI'

      CALL ISPFFV(6,'ZATR C',RC,ZATR,4)
      CALL ISPFFV(6,'ZF01 C',RC,ZF01,4)
      CALL ISPFFV(6,'ZF02 C',RC,ZF02,4)
      CALL ISPFFV(6,'ZF03 C',RC,ZF03,4)
      CALL ISPFFV(6,'ZF04 C',RC,ZF04,4)
      CALL ISPFFV(6,'ZF10 C',RC,ZF10,4)
      CALL ISPFFV(6,'ZCMD C',RC,ZCMD,4)

c
c     set function for keys
c
      ZF01='ADDI'
      ZF02='CONT'
      ZF10='QUIT'


c
c     Nullify Z commands
c

      ZCMD='    '
```

```
c
c     Display input screen one along with keys1 appearing
c     at the bottom
c


      CALL ISPFF(13,'DISPLAY KEYS1',RC)
      CALL ISPFF(11,'DISPLAY SP1',RC)
c
c     Look for user's responce
c


      IF(ZCMD.EQ.'ADDI') GOTO 170
      IF(ZCMD.EQ.'CONT') GOTO 152
      IF(ZCMD.EQ.'QUIT') GOTO 155

      GOTO 152

 172  ZF10='QUIT'
      ZCMD='    '
      ZATR='WRI'

      ZF10='QUIT'
      ZF01='RUN'
      ZCMD='    '


c
c   Display keys3 and additional screen for inputs.
c


      CALL ISPFF(13,'DISPLAY KEYS3',RC)
      CALL ISPFF(11,'DISPLAY SP3',RC)

c
c    Look for user's responce
c

      IF(ZCMD.EQ.'QUIT') GOTO 155
      IF(ZCMD.EQ.'RUN') GOTO 171

      GOTO 155

 173  ZF10='QUIT'
      ZCMD='    '
      ZATR='WRI'

      ZF10='QUIT'
      ZF01='RUN'
      ZF03='DES'
      ZCMD='    '
```

```
c
c     Display screen of output (design summary)
c

      CALL ISPFF(13,'DISPLAY KEYS5',RC)
      CALL ISPFF(12,'DISPLAY VEN3',RC)

c
c     look for user's responce.
c

      IF(ZCMD.EQ.'QUIT') GOTO 155
      IF(ZCMD.EQ.'RUN') GOTO 171
      IF(ZCMD.EQ.'DES') GOTO 172

      GOTO 155

 170  ZF10='QUIT'
      ZCMD='    '
      ZATR='WRI'

      ZF10='QUIT'
      ZF01='PREV'
      ZF02='CONT'

      ZCMD='    '

      CALL ISPFF(13,'DISPLAY KEYS4',RC)
      CALL ISPFF(11,'DISPLAY SP4',RC)

      IF(ZCMD.EQ.'QUIT')GOTO 155
      IF(ZCMD.EQ.'PREV') GOTO 171
      IF(ZCMD.EQ.'CONT') GOTO 152

      GOTO 152

 174  ZF10='QUIT'
      ZCMD='    '
      ZATR='WRI'

      ZF01='DES'
      ZF10='QUIT'
      ZF03='FIN'
      ZF04='RUN'

       ZCMD='    '

      CALL ISPFF(13,'DISPLAY KEYS2',RC)
      CALL ISPFF(11,'DISPLAY SP2',RC)

      IF(ZCMD.EQ.'QUIT') GOTO 155
      IF(ZCMD.EQ.'RUN') GOTO 171
      IF(ZCMD.EQ.'DES') GOTO 172
```

```
      IF(ZCMD.EQ.'FIN') GOTO 173
c
c     Main program to call different subroutines.
c
c

 152  CALL TAUVSXA()
      CALL AIRPROP()
      CALL HEAT()
      TAUA=TAUA*3600.0
      CALL INITIAL ()
      ANT=NTA
      ALT=ALF/100.0
      ABED=2*DBED/100.0
      AVELB=VELBR/100.0
      DB=DB/100.0
      WRITE(7,*)'ATAU =',ATAU,'HRS'
      CALL PCVOL()
 153  CALL FINAL1()
 154  ANAF=ANA0*(1-XAA)
      ANCF=ANC0 + ANA0*XAA
      TAUA=TAUA/3600
      CALL HEATEX(DELTAT)
      GOTO 174
      STOP
 155  END
```

APPENDIX B

LISTING FOR SUBROUTINES

```
      SUBROUTINE TAUVSXA()

      COMMON /Z1/ XA,TEMP,PRESS,PITCH,DHE
      COMMON /Z2/ TAUA,ANA0,ANB0,ANC0
      COMMON /Z3/ DOR,ANOR,DB,DBED,ALF,AKL
      COMMON /Z4/ VELBR,VELB,PHIL,NTA,U
      COMMON /Z5/ DELTA,TI,TC,NI,NU,RPFR
      COMMON /Z6/ XAA,DELHR,U0,AMDOT,TOUT,TIN
      COMMON /Z7/ DENG,TCG,VISG,GASCP,PRANG,DAB
      COMMON /Z8/ RATEK,CATDIA,CATDEN,EPSMF,VMF,EPSM,CATCP

C*************************************************************
C       THIS PROGRAM IS USED TO EVALUATE THE RATE EXPRESSION
C       FOR THE DI-METHYL TEREPHTHALATE REACTION FROM P-XYLENE.
C       THE CONVERSION AND WASHOUT FUNCTION WHERE STUDIED AS A
C       FUNCTION OF RESIDENSE TIME.
C*************************************************************
C       THE FOLLOWING RATE EXPRESSION(S) WHERE ADOPTED.
C
C       -rA=d[px]/dt=2.55e-05 [px]^2 [co]^0.21/[PMT]
C
C
C************************************************************* *
C       FILES
C
C       PC.DAT IS THE OUTPUT FOR A CSTR (XA VS TAU)
C       PP.DAT IS THE OUTPUT FOR A PFR  (XA VS TAU)
C       RESC.DAT FOR CSTR (W(T) VS TAU)
C       RESP.DAT FOR PFR  (W(T) VS TAU)
C
C************************************************************ ***
      OPEN(12,FILE='PC.DAT',STATUS='UNKNOWN')
      OPEN(13,FILE='PP.DAT',STATUS='UNKNOWN')
      OPEN(14,FILE='RESC.DAT',STATUS='UNKNOWN')
      OPEN(15,FILE='RESP.DAT',STATUS='UNKNOWN')

C************************************************************ ****
C       NOMENCLATURE USED
C
C       XA=CONVERSION OF P-XYLENE
C       VOL=VOLUME OF THE REACTOR
C       D=DIAMETER OF REACTOR
C       AL=LENGTH OF REACTOR
C       ANA0=INITIAL NUMBER OF MOLES OF P-XYLENE
C       ANB0=INITIAL NUMBER OF MOLES OF COBALT
C       ANC0=INITIAL NUMBER OF MOLES OF TEREPHTHALIC ACID
C       CA0,CB0,CC0=INITIAL CONC. OF PX,CO,TA
C       TAU=RESIDENSE TIME
C       RA=RATE EXPRESSION FOR CSTR CONVERSION.
C       WT=WASH OUT TIME   =    (CA(T)-CAF)/(CA0-CAF)
C
C
C*************************************************************
```

```
      RATEK=2.5E-05*((273+TEMP)/(273+140))

      CA0=10.0
      CB0=10.1
      CC0=1.0

      AM=CB0/CA0
      AN=CC0/CA0

      DO 10 TAU=1,75000,1800

      DO 20 I=1,9800,100
      AXA=I*.0001
      AA=RATEK*(CA0**2*(1-AXA)**2.)*(CB0)**0.21
      BB=(CC0+AXA*CA0)
      RA=AA/BB
      TAUC=CA0*AXA/RA
      IF(ABS(TAUC/TAU - 1.).LT.0.05) GOTO 500
20    CONTINUE

      GOTO 101
500   WRITE(12,*)TAU/3600,AXA
      CA=CA0*(1.- AXA)
      CAF=CA0*(1. - .98)
      WT=(CA-CAF)/(CA0-CAF)
      WRITE(14,*)TAU/3600,WT
101   DO 30 I=1,9800,100
      AXA=I*.0001
      RATE=(AN+1)*(1/(1-AXA) -1.0)+LOG(1 - AXA)
      TAUP=CA0*RATE/(RATEK*CA0**1.21*AM**0.21)
      IF(ABS(TAUP/TAU - 1.).LT.0.05) GOTO 600
30    CONTINUE
      GOTO 10
600   WRITE(13,*)TAU/3600,AXA
      CA=CA0*(1-AXA)
      CAF=CA0*(1.-.98)
      WT=(CA-CAF)/(CA0-CAF)
      WRITE(15,*)TAU/3600,WT
10    CONTINUE
      RETURN
      END


      SUBROUTINE TAUEST(XXA)

C*****************************************************************
C     This subroutine is used to estimate the conversion for a
C     given residence time.  The average conversion for the CSTR
C     and a plug flow reactor is taken as the conversion in a
C     bubble column.
C*****************************************************************

      COMMON /Z1/ XA,TEMP,PRESS,PITCH,DHE
      COMMON /Z2/ TAUA,ANA0,ANB0,ANC0
```

```
      COMMON /Z3/ DOR,ANOR,DB,DBED,ALF,AKL
      COMMON /Z4/ VELBR,VELB,PHIL,NTA,U
      COMMON /Z5/ DELTA,TI,TC,NI,NU,RPFR
      COMMON /Z6/ XAA,DELHR,U0,AMDOT,TOUT,TIN
      COMMON /Z7/ DENG,TCG,VISG,GASCP,PRANG,DAB
      COMMON /Z8/ RATEK,CATDIA,CATDEN,EPSMF,VMF,EPSM,CATCP


C************************************************************ ****
C       NOMENCLATURE USED
C
C       XA=CONVERSION OF P-XYLENE
C       VOL=VOLUME OF THE REACTOR
C       D=DIAMETER OF REACTOR
C       AL=LENGTH OF REACTOR
C       ANA0=INITIAL NUMBER OF MOLES OF P-XYLENE
C       ANB0=INITIAL NUMBER OF MOLES OF COBALT
C       ANC0=INITIAL NUMBER OF MOLES OF TEREPHTHALIC ACID
C       CA0,CB0,CC0=INITIAL CONC. OF PX,CO,TA
C       TAU=RESIDENSE TIME
C       RA=RATE EXPRESSION FOR CSTR CONVERSION.
C       WT=WASH OUT TIME   =    (CA(T)-CAF)/(CA0-CAF)
C
C
C************************************************************ ***

      CA0=10
      CB0=10.1
      CC0=1

      DO 121 II=1,9800,20
      XXA=0.0001*II
      AM=CB0/CA0
      AN=CC0/CA0
      AA=RATEK*(CA0**2*(1-XXA)**2)*(CB0)**0.21
      BB=(CC0+XXA*CA0)
      RA=AA/BB
      TAUC=CA0*XXA/RA
      IF(ABS(TAUA/TAUC - 1).LT.0.05) GOTO 124
121   CONTINUE

124   XAC=XXA


      DO 126 II=1,9800,10
      XXA=0.0001*II
      RATE=(AN+1)*(1/(1-XXA)-1)-  LOG(1-XXA)
      TAUP=CA0*RATE/(RATEK*CA0**1.21*AM**0.21)
      IF(ABS(TAUA/TAUP - 1).LT. 0.05) GOTO 127
126   CONTINUE

127   XAP=XXA

      XXA=(XAP+XAC)/2
```

```
      RETURN
      END

      SUBROUTINE INITIAL()

      COMMON /Z1/ XA,TEMP,PRESS,PITCH,DHE
      COMMON /Z2/ TAUA,ANA0,ANB0,ANC0
      COMMON /Z3/ DOR,ANOR,DB,DBED,ALF,AKL
      COMMON /Z4/ VELBR,VELB,PHIL,NTA,U
      COMMON /Z5/ DELTA,TI,TC,NI,NU,RPFR
      COMMON /Z6/ XAA,DELHR,U0,AMDOT,TOUT,TIN
      COMMON /Z7/ DENG,TCG,VISG,GASCP,PRANG,DAB
      COMMON /Z8/ RATEK,CATDIA,CATDEN,EPSMF,VMF,EPSM,CATCP

C*************************************************************
C     THIS PROGRAM DESIGNA REACTOR TO HANDLE THE INPUT
C     REQUIREMENTS FOR THEOXIDATION OF P-XYLENE TO PMT.
C*************************************************************
      TOTPROD=120.0
      VOLFRAC=0.75
C*************************************************************
C     THREE MOLES OF AIR PER MOLE OF P-XYLENE IS TO BE SUPPLIED FOR
C     THE ABOVE REACTION.
C*************************************************************
      AIRFLOW=TOTPROD*3.0*1000/3600

C*************************************************************
C     NOMENCLATURE
C
C     SPAREA=TOTAL SPARGER AREA CM*CM
C     AIRVOL=VOLUMETRIC FLOW RATE OF AIR THROUGH SPARGER CM**3/SEC
C     UOR=VELOCITY OF BUBBLE AT THE ORIFICE CM/SEC
C     U0=SUPERFICIAL GAS VELOCITY
C     DB=DIAMETER OF BUBBLE
C*************************************************************
      FACTOR1=ANA0/120.0

      AIRVOL=AIRFLOW*22414*(TEMP+273)/273/PRESS

      SPAREA=3.14*DOR**2/4*ANOR

      UOR=AIRVOL/SPAREA

      CALL TAUEST(XXA)

      XA=XXA
      WRITE(6,*)'XA=',XA
      WRITE(7,*)'U0=',U0,' CMS/SEC'
C
C     Calculate diameter of bubble.
C
      DB=117*((UOR/100)**0.4)*(DOR/100)**0.8/(9.81**0.2)
      WRITE(7,*)'DB=',DB,' CMS'
```

```
C*************************************************************
C       NOMENCLATURE
C
C       RATEK=RATE CONSTANT OF REACTION
C       CATDIA=DIAMETER OF CATALYST (M)
C       CAPCP=SPECIFIC HEAT OF CATALYST CAL/GM.DEGREE C
C       CATDEN=DENSITY OF CATALYST GM/CC
C       EPSM=VOID FRACTION IN A PACKED BED
C       EPSMF=VOID FRACTION UNDER MINIMUM FLUIDISING CONDITIONS
C       VMF=FLUIDISATION VELOCITY CM/SEC
C       DENG= DENSITY OF GAS GM/CC
C       TCG=THERMAL CONDUCTIVITY OF GAS CAL/CM.SEC.DEGREE C
C       PRANG=PRANDL'S NUMBER OF GAS
C       VISG=VISCOSITY OF GAS GM/CM.SEC.
C       GASCP=SPECIFIC HEAT OF GAS
C       DAB=DIFFUSION COEFFICIENT CM*CM/SEC
C       XA=CONVERSION
C       FTUBE=FRACTION NOT OCCUPIED BY TUBES
C       DBED=DIAMETER OF BED (CM)
C       NT=NUMBER OF TUBES
C       NTA= ACTUAL NUMBER OF TUBES
C       VELB=VELOCITY OF BUBBLE CM/SEC
C*************************************************************

c
c       Calculate fraction of bed not occupied by tybes.
c

        FTUBE=(0.5*((3**0.5)/2)*(PITCH**2)-0.5*(3.14/4)*(DHE**2))
        DAM=(0.5*(3**0.5)/2*(PITCH**2))
        FTUBE=FTUBE/DAM
        WRITE(7,*)'FRACTION NOT OCCUPIED BY TUBES',FTUBE

c
c       Calculate diameter of bed required.
c

        DT2=(AIRVOL)*4/(3.14*FTUBE)/U0
        DBED=1.1*SQRT(DT2)
        WRITE(7,*)'DT=',DBED,' CMS'

        NT=(3.14/4)*DT2/(2*0.5*(3**0.5)*PITCH*PITCH/2)
        WRITE(7,*)'NT=',NT,' TUBES'
c
c       Calculate velocity of bubble.
c

        VELB=U0-VMF+(0.711*(980*DB)**0.5)
        VELBR=.711*(980*DB)**0.5

        WRITE(7,*)'BUBBLE  VELOCITY',VELB,' CM/SEC'
        ADELTA=(U0-VMF)/VELB
```

```
c       Calculate mass transfer coefficient(akl),
c        liquid mixing (phil)
c

        VLc=0.9*(9.81*DBED/100*U0/100)**0.333
        DEl=.37*DBED/100*VLc
        DEg=78*(U0/100*DBED/100)**1.5
        DL=(DEl+DEg)/2
        AKl=1.13*((VELB-U0-VMF)*DL/DB)**0.5
        PHIL=0.30*(DBED/100)**1.66*(AIRVOL/1E06)**0.33*9.81**0.33

        WRITE(7,*)'THE MASS TRANSFER COEFFT. Kl IS',AKL,' M/SEC'
        WRITE(7,*)'THE LIQUID MIXING IS ',PHIL,' M**3/SEC'

        BCB=4.5*(VMF/DB)+5.85*((DAB**0.5)*(980**0.25))/(DB**1.24)
        CEB=6.78*(((VMF*DAB*VELB)/(DB**3))**0.5)

        AKF=-LOG(1-XA)

c
c       Calculating the ratios gammaA etc.
c


        GAMB=(1-EPSMF)*(1-ADELTA)*0.015/ADELTA
        ALPHA=0.6
        AAA=3*VMF/EPSMF
        BBB=0.711*(980*DB)**0.5-(VMF/EPSMF)
        GAMC=(1-EPSMF)*(AAA/BBB + ALPHA)
        GAME=((1-ADELTA)/ADELTA)*(1-EPSMF)-(GAMB+GAMC)
        AAAA=1/(RATEK/CEB+1/GAME)
        BBBB=1/(AAAA+GAMC)
        CC=1/(RATEK/BCB+BBBB)+GAMB

c
c      Calculating length of reactor needed
c

        ALF=VELB*AKF/(RATEK*CC)/12/3600
        ALM=ALF*(1-ADELTA)*(1-EPSMF)/(1-EPSM)

        TDH=1.3*DBED

c
c       Calculating the overall heat transfer coefficient.
c

        RET=DBED*DENG*U0/VISG
        CD=0.42
        AAAAA=(1-EPSM)*ALM/ALF
        BBBBB=GASCP*DENG/TCG
        REP=CATDIA*DENG*U0/VISG
        CR=0.01844*1.5*AAAAA*(BBBBB**0.43)*(REP**0.23)
        CR=CR*((CATCP/GASCP)**0.8)*((CATDEN/DENG)**0.66)
```

```
      HW=CR*TCG/CATDIA
      OU=1/HW+1/0.0833+1/0.044
      U=1/OU
      WRITE(7,*)'THE OVERALL HEAT TRANSFER COEFFT. IS ',U

c
c     Calculate heat released.
c

      HEAT=(AIRFLOW)*XA*DELHR

c
c     Calculate actual number of tubes needed.
c

      NTA=HEAT/(3.14*DHE*ALF*U*100)
      WRITE(7,*)'ACTUAL NUMBER OF TUBES NEEDED IS',NTA,' TUBES'
      ALF=FACTOR1*ALF
      WRITE(7,*)'HEIGHT OF REACTOR REQUIRED',ALF,' CMS'

      RETURN
      END

      SUBROUTINE PCVOL()

c*************************************************************
c     This subroutine calculate the core of the reactor not
c     occupied by tubes.
c*************************************************************

      DIMENSION R(100)

      COMMON /Z1/ XA,TEMP,PRESS,PITCH,DHE
      COMMON /Z2/ TAUA,ANA0,ANB0,ANC0
      COMMON /Z3/ DOR,ANOR,DB,DBED,ALF,AKL
      COMMON /Z4/ VELBR,VELB,PHIL,NTA,U
      COMMON /Z5/ DELTA,TI,TC,NI,NU,RPFR
      COMMON /Z6/ XAA,DELHR,U0,AMDOT,TOUT,TIN
      COMMON /Z7/ DENG,TCG,VISG,GASCP,PRANG,DAB
      COMMON /Z8/ RATEK,CATDIA,CATDEN,EPSMF,VMF,EPSM,CATCP
c
c     TI = time required for the bubble to reach top of reactor.
c

      TI=ALF/VELBR
      TC=TI
c
c     Number of cycles

      NU=TAUA/TI
c
c     Number of segments

      NI=ALF/DELTA
```

```
      WRITE(7,*)'NU=',NU,'NI=',NI
      TA=3.14*(DBED)**2/4

      QTA=TA/4
c*******************************************************
c                   NOMENCLATURE USED
c     arcl = arc length
c     ntarc = number of tubes in arc.
c     ntaa = actual number of tubes.
c*******************************************************

      NTAA=NTA/2
      WRITE(7,*)'NTAA=',NTAA
      RBED=DBED/2
      R(1)=RBED

      NTARC=0

      DO 25 I=2,100
c
c     Assume only one thirds of the reactor radius is
c     occupied by tubes
c

      ARCL=.65*3.14*R(I-1)
      NTARC=ARCL/PITCH + (NTARC+1)
      IF (NTARC.GT.NTAA) GOTO 129
      R(I)=R(I-1) - SQRT(PITCH**2-(0.5*PITCH)**2)
 25   CONTINUE

 129  RPFR=R(I-1)

      WRITE(7,*)'PLUG FLOW CHANNEL RADIUS = ',RPFR,'  CMS'

      RETURN
      END



      SUBROUTINE FINAL1()

c*************************************************************
c     This subroutine calculates the final conversion for the
c     reaction based on the design and other criteria.
c
c*************************************************************

      COMMON /Z1/ XA,TEMP,PRESS,PITCH,DHE
      COMMON /Z2/ TAUA,ANA0,ANB0,ANC0
      COMMON /Z3/ DOR,ANOR,DB,DBED,ALF,AKL
      COMMON /Z4/ VELBR,VELB,PHIL,NTA,U
      COMMON /Z5/ DELTA,TI,TC,NI,NU,RPFR
      COMMON /Z6/ XAA,DELHR,U0,AMDOT,TOUT,TIN
      COMMON /Z7/ DENG,TCG,VISG,GASCP,PRANG,DAB
```

```
      COMMON /Z8/ RATEK,CATDIA,CATDEN,EPSMF,VMF,EPSM,CATCP
c
c     initialize concentration.

      CALL INCONC(CA0,CB0,CC0)

      AM=CB0/CA0
      AN=CC0/CA0
      CA00=CA0
      CAP0=CA0
c                    Nomenclature used
c
c     PFRVOL = Plug flow reactor volume.
c     CSTRVOL = CSTR volume
c

      PFRVOL=3.14*RPFR**2*ALF
      CSTRVOL=3.14*DBED**2*ALF/4 - PFRVOL -NTA*3.14*DHE**2*ALF/4

      DO 32 I=1,NU

      DO 33 J=1,NI
c
c     calculate velocity
c

      VEL=VELB*(1.005)**(J-1)
      TP=DELTA/VEL

C*************************************************************** ****
C     NOMENCLATURE USED
C
C     XA=CONVERSION OF P-XYLENE
C     VOL=VOLUME OF THE REACTOR
C     D=DIAMETER OF REACTOR
C     AL=LENGTH OF REACTOR
C     ANA0=INITIAL NUMBER OF MOLES OF P-XYLENE
C     ANB0=INITIAL NUMBER OF MOLES OF COBALT
C     ANC0=INITIAL NUMBER OF MOLES OF TEREPHTHALIC ACID
C     CA0,CB0,CC0=INITIAL CONC. OF PX,CO,TA
C     TAU=RESIDENSE TIME
C     RA=RATE EXPRESSION FOR CSTR CONVERSION.
C
C
C*************************************************************** ***

      DO 301 II=1,10000,20
      BXA=II*.0001
      RATE=(AN + 1)*(1/(1-BXA) -1.0)+LOG(1-BXA)
      TAUP=CAP0*RATE/(RATEK*CAP0**1.21*AM**0.21)
      IF(ABS(TAUP/TP - 1.).LT.0.1) GOTO 12
 301  CONTINUE
c
c
```

```
c       Reducing the conversion on a volumetric basis
c       This is for the core of length delta (PFR).

 12     BXA=BXA*PFRVOL/(CSTRVOL + PFRVOL)*DELTA/ALF
        CAP0=CAP0*(1-BXA)
        IF(J.EQ.1)THEN
        CA0PB=CAP0
        ELSE IF(J.EQ.NI) THEN
        CA0PT=CAP0
        ENDIF
 33     CONTINUE
        CAC00=(CA0PB)
        CAC0=CAC00

c
c       Calculation for CSTR
c
        DO 21 III=1,10000,20
        BXA=III*.0001
        AA=RATEK*(CAC0**2*(1-BXA)**2.)*(CB0)**0.21
        BB=(CC0+BXA*CAC0)
        RA=AA/BB
        TAUC=CAC0*BXA/RA
        IF(ABS(TAUC/TI - 1.).LT.0.1) GOTO 501
 21     CONTINUE
 501    BXA=BXA*CSTRVOL/(CSTRVOL + PFRVOL)*DELTA/ALF
        CAC0=CAC0*(1.- BXA)
        PFRVOL=3.14*RPFR**2*ALF
        CSTRVOL=3.14*DBED**2*ALF/4 - PFRVOL -NTA*3.14*DHE**2*ALF/4
c
c       Calculate new concentration for the next cycle.
c
        CAP0=((CAC00+CAC0)/2*CSTRVOL+(CA0PB+CA0PT)/2*PFRVOL)
     +   /(CSTRVOL+PFRVOL)
 32     CONTINUE
C*****************************************************************
c
c      Final conversion  is XAA
c

        XAA=(CA00-CAP0)/CA00
        WRITE(7,*)'FINAL XA=',XAA

        RETURN
        END



        SUBROUTINE AIRPROP()

c       This subroutine calculates the air properties at a
c       given temperature and pressure.  These values are used
c       other subroutines.
c
```

```
      COMMON /Z1/ XA,TEMP,PRESS,PITCH,DHE
      COMMON /Z2/ TAUA,ANA0,ANB0,ANC0
      COMMON /Z3/ DOR,ANOR,DB,DBED,ALF,AKL
      COMMON /Z4/ VELBR,VELB,PHIL,NTA,U
      COMMON /Z5/ DELTA,TI,TC,NI,NU,RPFR
      COMMON /Z6/ XAA,DELHR,U0,AMDOT,TOUT,TIN
      COMMON /Z7/ DENG,TCG,VISG,GASCP,PRANG,DAB
      COMMON /Z8/ RATEK,CATDIA,CATDEN,EPSMF,VMF,EPSM,CATCP

      TEMPK= 273 + TEMP

      ACTVOL=22414/273*TEMPK/( PRESS )
      DENG=(.79*28 + .21*32)/ACTVOL
      GASCP=(6.713 + 0.04697E-02*(TEMPK-273)
     +    +0.1147E-05*(TEMPK-273)**2 -0.4696E-09*(TEMPK-273)**3)/28.84
      TCG=1.3E-04*(TEMPK/273)**.5
      VISG=4.0E-04*(273/TEMPK)**.33

      RETURN
      END

      SUBROUTINE HEAT()

      COMMON /Z1/ XA,TEMP,PRESS,PITCH,DHE
      COMMON /Z2/ TAUA,ANA0,ANB0,ANC0
      COMMON /Z3/ DOR,ANOR,DB,DBED,ALF,AKL
      COMMON /Z4/ VELBR,VELB,PHIL,NTA,U
      COMMON /Z5/ DELTA,TI,TC,NI,NU,RPFR
      COMMON /Z6/ XAA,DELHR,U0,AMDOT,TOUT,TIN
      COMMON /Z7/ DENG,TCG,VISG,GASCP,PRANG,DAB
      COMMON /Z8/ RATEK,CATDIA,CATDEN,EPSMF,VMF,EPSM,CATCP
c
c     DELHR is the heat of reaction.
c

      DELHR=3.25e03 +0.25*(TEMP-140) +1.25*(TEMP-140)

      RETURN
      END


      SUBROUTINE INCONC(CA0,CB0,CC0)

*******************************************************
c     This program calculates the concentration of
c     reactants. This value gets changed elsewhere
c     in the program so this re initializes each time.
c*******************************************************

      COMMON /Z1/ XA,TEMP,PRESS,PITCH,DHE
      COMMON /Z2/ TAUA,ANA0,ANB0,ANC0
      COMMON /Z3/ DOR,ANOR,DB,DBED,ALF,AKL
      COMMON /Z4/ VELBR,VELB,PHIL,NTA,U
      COMMON /Z5/ DELTA,TI,TC,NI,NU,RPFR
```

```
      COMMON /Z6/ XAA,DELHR,U0,AMDOT,TOUT,TIN
      COMMON /Z7/ DENG,TCG,VISG,GASCP,PRANG,DAB
      COMMON /Z8/ RATEK,CATDIA,CATDEN,EPSMF,VMF,EPSM,CATCP
      VOL=(3.14*(DBED/100)**2/4 -NTA*3.14*(DHE/100)**2/4)*ALF/100
      CA0=ANA0/VOL
      CB0=ANB0/VOL
      CC0=ANC0/VOL
      RETURN
      END

      SUBROUTINE HEATEX(DELTAT)
C
C     This subroutine is included for future development
C     for the heat exchanger.
C
      COMMON /Z1/ XA,TEMP,PRESS,PITCH,DHE
      COMMON /Z2/ TAUA,ANA0,ANB0,ANC0
      COMMON /Z3/ DOR,ANOR,DB,DBED,ALF,AKL
      COMMON /Z4/ VELBR,VELB,PHIL,NTA,U
      COMMON /Z5/ DELTA,TI,TC,NI,NU,RPFR
      COMMON /Z6/ XAA,DELHR,U0,AMDOT,TOUT,TIN
      COMMON /Z7/ DENG,TCG,VISG,GASCP,PRANG,DAB
      COMMON /Z8/ RATEK,CATDIA,CATDEN,EPSMF,VMF,EPSM,CATCP

      HTREL=1000*ANA0*XA*DELHR/TAUA*3600
      CPWATER=1.0
      DELTAT=100
      TOUT=TIN + 100.0
      AMDOT=HTREL/CPWATER/DELTAT/1000/3600
      RETURN
      END
```

APPENDIX C

PROGRAM LISTING FOR GRAPHICS

```
/*  This program written in C provides graphics for the first */
/*  two screens */

#ifdef __TINY__
#error display will not run in the tiny model.
#endif

#include <dos.h>
#include <math.h>
#include <conio.h>
#include <stdio.h>
#include <stdlib.h>
#include <stdarg.h>

#include <graphics.h>

#define ESC     0x1b                    /* Define the escape key        */
#define TRUE    1                       /* Define some handy constants  */
#define FALSE   0                       /* Define some handy constants  */
#define PI      3.14159                 /* Define a value for PI        */
#define ON      1                       /* Define some handy constants  */
#define OFF     0                       /* Define some handy constants  */

char *Fonts[] = {
  "DefaultFont",   "TriplexFont",   "SmallFont",
  "SansSerifFont", "GothicFont"
};

char *LineStyles[] = {
  "SolidLn",  "DottedLn",  "CenterLn",  "DashedLn",  "UserBitLn"
};

char *FillStyles[] = {
  "EmptyFill",  "SolidFill",      "LineFill",      "LtSlashFill",
  "SlashFill",  "BkSlashFill",    "LtBkSlashFill", "HatchFill",
  "XHatchFill", "InterleaveFill", "WideDotFill",   "CloseDotFill"
};

char *TextDirect[] = {
  "HorizDir",  "VertDir"
};

char *HorizJust[] = {
  "LeftText",   "CenterText",   "RightText"
};

char *VertJust[] = {
  "BottomText",  "CenterText",  "TopText"
};
 int i,j;
 int r[100],x[100],y[100];
 int mradius;
 int betax,betay,gammax,gammay;
struct PTS {
```

```
  int x, y;
};      /* Structure to hold vertex points      */

int    GraphDriver;             /* The Graphics device driver          */
int    GraphMode;               /* The Graphics mode value             */
double AspectRatio;             /* Aspect ratio of a pixel on the screen*/
int    MaxX, MaxY;              /* The maximum resolution of the screen */
int    MaxColors;               /* The maximum # of colors available    */
int    ErrorCode;               /* Reports any graphics errors         */
struct palettetype palette;             /* Used to read palette info    */

/*                                                                      */
/*      Function prototypes                                             */
/*                                                                      */

void Initialize(void);
void LineRelDemo(void);
void LineToDemo(void);
void CRTModeDemo(void);
void FillStyleDemo(void);
void FillPatternDemo(void);
void PaletteDemo(void);
void PolyDemo(void);
void changetextstyle(int font, int direction, int charsize);
int  gprintf(int *xloc, int *yloc, char *fmt, ... );
void inti();
void pausef();
void copyright(void);
void changetextstyle(int font, int direction, int charsize);
void pause(void);

/*                                                                      */
/*      Begin main function                                             */
/*                                                                      */

int main()
{

Initialize();                /* Set system into Graphics mode       */
if( GraphDriver==EGA || GraphDriver==EGALO || GraphDriver==VGA ) LineRelDemo();
closegraph();                /* Return the system to text mode      */
return(0);
}

/*                                                                       */
/*      INITIALIZE: Initializes the graphics system and reports          */
/*      any errors which occured.                                        */
/*                                                                       */

void Initialize(void)
{
int xasp, yasp;                      /* Used to read the aspect ratio*/

GraphDriver = DETECT;                /* Request auto-detection      */
```

```
initgraph( &GraphDriver, &GraphMode, "" );
ErrorCode = graphresult();            /* Read result of initialization*/
if( ErrorCode != grOk ){              /* Error occured during init    */
printf(" Graphics System Error: %s\n", grapherrormsg( ErrorCode ) );
exit( 1 );
  }

getpalette( &palette );               /* Read the palette from board  */
MaxColors = getmaxcolor() + 1;        /* Read maximum number of colors*/

MaxX = getmaxx();
MaxY = getmaxy();                     /* Read size of screen          */

getaspectratio( &xasp, &yasp );       /* read the hardware aspect     */
AspectRatio = (double)xasp / (double)yasp; /* Get correction factor   */

}


/*                                                                     */
/*      LINERELDEMO: Display pattern using moverel and linerel cmds.   */
/*                                                                     */

void LineRelDemo(void)
{
struct viewporttype vp;
int h, w, dx, dy, cx, cy;
struct PTS outs[7];



getviewsettings( &vp );



setfillstyle( SOLID_FILL, 6 );
bar( 0, 0, vp.right-vp.left, vp.bottom-vp.top );      /* Draw backgnd */
setcolor(BLACK);
gammay=MaxY/10;
copyright();
setfillstyle( SOLID_FILL, RED );
bar( 0, 0, vp.right-vp.left, vp.bottom-vp.top );      /* Draw backgnd */
setcolor(BLACK);
changetextstyle(TRIPLEX_FONT,HORIZ_DIR,4); settextjustify(CENTER_TEXT,TOP_TEXT);
outtextxy(MaxX/2,10,"S P A R G E R  R E A C T O R");
betax =( MaxX )/2;
betay =( MaxY) /2;
gammay=MaxY/10;
changetextstyle(TRIPLEX_FONT,HORIZ_DIR,1);
settextjustify(CENTER_TEXT,TOP_TEXT);
outtextxy(betax + betax/2,MaxY -8*gammay,"Sparger reactors are bubble");
settextjustify(CENTER_TEXT,TOP_TEXT);
outtextxy(betax + betax/2,MaxY -7*gammay,"columns and are used in the");
```

```
settextjustify(CENTER_TEXT,TOP_TEXT);
outtextxy(betax + betax/2,MaxY -6*gammay,"manufacture of DMT used as a raw");
settextjustify(CENTER_TEXT,TOP_TEXT);
outtextxy(betax + betax/2,MaxY -5*gammay,"material for polymers like nylon.");
changetextstyle(TRIPLEX_FONT,HORIZ_DIR,2);
settextjustify(CENTER_TEXT,TOP_TEXT);
outtextxy(betax + betax/2,MaxY - 4*gammay,"OPERATING CONDITIONS");
changetextstyle(TRIPLEX_FONT,HORIZ_DIR,1);
settextjustify(CENTER_TEXT,TOP_TEXT);
outtextxy(betax + betax/2,MaxY - 3*gammay,"Temperature: 140 - 170½ C");
settextjustify(CENTER_TEXT,TOP_TEXT);
outtextxy(betax + betax/2,MaxY - 2*gammay,"Pressure:  4 - 8 atms.");
setcolor(BLUE);
changetextstyle(TRIPLEX_FONT,HORIZ_DIR,1);
outtextxy(MaxX/2,MaxY -25,"Press any key to continue");
setcolor(WHITE);
line(50,MaxY -40,MaxX/2 - 50,MaxY -40);
line(50,80,MaxX/2 - 50,80);
line(50,80,50,MaxY - 40);
line(MaxX/2 - 50,80,MaxX/2 -50,MaxY - 40);

line(40,100,80,100);
line(80,100,80,MaxY - 60);
line(80,MaxY -60,40,MaxY - 60);
line(40,107,70,107);
line(70,107,70,MaxY -68);
line(70,MaxY -68,40,MaxY -68);


line(MaxX/2 - 40,100,MaxX/2 -80,100);
line(MaxX/2 -80,100,MaxX/2 -80,MaxY -60);
line(MaxX/2 -80,MaxY -60,MaxX/2 -40,MaxY -60);
line(MaxX/2 -40,107,MaxX/2 -70,107);
line(MaxX/2 -70,107,MaxX/2 -70,MaxY -68);
line(MaxX/2 -70,MaxY -68,MaxX/2 -40,MaxY -68);

line(MaxX/2 -220,MaxY -67,MaxX/2 -90,MaxY - 67);
line(MaxX/2 -155,MaxY -67,MaxX/2 -155,MaxY -30);
mradius = 10;
while ( !kbhit()) {
        for(j = 1;j<=20;j++) {
setcolor(WHITE);
         x[j] = MaxX/2 - 225 + random(MaxX/2 -190);
         y[j] = MaxY -90 - random(MaxY -187);
         r[j] = random(mradius);

circle(x[j],y[j],r[j]);
               }
setcolor(RED);
       for(j = 1;j<=30;j++)
    circle(x[j],y[j],r[j] );
        }
restorecrtmode();
        pausef();
```

```
        }

void changetextstyle(int font, int direction, int charsize)
{
  int ErrorCode;

graphresult();                          /* clear error code            */
settextstyle(font, direction, charsize);
ErrorCode = graphresult();              /* check result                */
if( ErrorCode != grOk ){                /* if error occured            */
closegraph();
printf(" Graphics System Error: %s\n", grapherrormsg( ErrorCode ) );
   exit( 1 );
  }
}

  void inti()
   {
    int g_driver,g_mode,g_error;
    detectgraph(&g_driver,&g_mode);
    if(g_mode == EGAHI)
    g_mode = EGALO;
    initgraph(&g_driver,&g_mode,"");
    g_error = graphresult();
     if(g_error < 0 )
      {
       printf("graphics system error: %s\n");
       exit(1);
       }
   }
  void copyright(void)
  {
  changetextstyle(TRIPLEX_FONT,HORIZ_DIR,4);
  settextjustify(CENTER_TEXT,TOP_TEXT);
  outtextxy(MaxX/2,20,"S P A R G E R  R E A C T O R");
  changetextstyle(3,HORIZ_DIR,4);
  outtextxy(MaxX/2,MaxY -7*gammay-30,"Modeled By:");
  changetextstyle(TRIPLEX_FONT,HORIZ_DIR,3);
  outtextxy(MaxX/2,MaxY -7*gammay,"W, Venkatesh");
  changetextstyle(TRIPLEX_FONT,HORIZ_DIR,1);
  outtextxy(MaxX/2,MaxY -3.5*gammay-60,"Master's Thesis (1992)");
  outtextxy(MaxX/2,MaxY -3.5*gammay-30,"School of Chemical Engineering");
  outtextxy(MaxX/2,MaxY-3.5*gammay,"Oklahoma State University");
  while ( !kbhit() ) {
  changetextstyle(TRIPLEX_FONT,HORIZ_DIR,1);
  outtextxy(MaxX/2,MaxY -30,"Press any key to continue");
                  }
  pause();
  cleardevice();
    }

void pause(void)
{
  int c;
```

```
  c = getch();                          /* Read a character from kbd    */


  if( 0 == c ){                         /* Did use hit a non-ASCII key? */

   c = getch();
  }


}

void pausef(void)
{
  int c;
c = getch();                           /* Read a character from kbd    */

  if( 0 == c ){                         /* Did use hit a non-ASCII key? */

   c = getch();
   closegraph();
  }


}
```

VITA

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